PB-213 639

PILOT SCALE UP OF PROCESSES TO DEMONSTRATE UTILIZATION OF PULVERIZED COAL FLYASH MODIFIED BY THE ADDITION OF LIMESTONE-DOLOMITE SULFUR DIOXIDE REMOVAL ADDITIVES

West Virginia University

Prepared for:

Environmental Protection Agency

October 1971

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U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-R-2-72-027	2. 124	3. Recipient's Accession No. PB-213 639
4. Title and Subtitle: Pilot Scale Up of Processes to Demonstrate Utilization of Pulverized Coal Flyash Modified by the Addition of Limestone-Dolomite Sulfur Dioxide Removal Additives			5. Report Date: October 1971 6.
7. Author(s)			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: Coal Research Bureau, School of Mines, West Virginia University, Morgantown, West Virginia 26505			10. Project/Task/Work Unit No. 11. Contract/Grant No. CPA 70-66
12. Sponsoring Organization Name and Address: ENVIRONMENTAL PROTECTION AGENCY, Office of Air Programs, Control Systems Division, Research Triangle Park, North Carolina 27711			13. Type of Report & Period Covered: Final 14.

15. Supplementary Notes

16. Abstracts: Bench-scale experiments to examine methods for potential utilization of modified flyash indicate that this ash, the solid by-product resulting from the limestone/dolomite process for fixing gaseous sulfur oxides as solid sulfates, can be considered a suitable raw material for a number of new products and processes. The most promising methods of utilization incorporating the total utilization of modified flyash are the production of calcium-silicate and cement-like structural products, high temperature production of materials such as mineral wool insulation and the use of modified flyash as a soil stabilizer and amendment. Other utilization areas were examined and are mentioned; also, several process problems and limitations are discussed.

17. Key Words and Document Analysis. 17a. Descriptors

Air Pollution
Flyash
Utilization
Construction Materials
Ceramic Materials
Calcium Silicates
Soil Stabilization
Mineral Wool
Stabilizers (agents)
Flotation
Bricks
Concretes

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13B

18. Availability Statement: Unlimited

19. Security Class (This Report) UNCLASSIFIED — 21. No. of Pages 108

20. Security Class (This Page) UNCLASSIFIED — 22. Price $3.00 $0.95

FORM NTIS-35 (REV. 3-72)
USCOMM-DC 14952-P72

PB 213 639

TECHNICAL REPORT

EPA-R2-72-027

PILOT SCALE UP OF PROCESSES TO DEMONSTRATE UTILIZATION OF PULVERIZED COAL FLYASH MODIFIED BY THE ADDITION OF LIMESTONE-DOLOMITE SULFUR DIOXIDE REMOVAL ADDITIVE

FINAL REPORT
CONTRACT CPA 70-66
ENVIRONMENTAL PROTECTION AGENCY OFFICE OF AIR PROGRAMS CONTROL SYSTEMS DIVISION

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109

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Coal Research Bureau
School of Mines
West Virginia University
Morgantown, West Virginia

FINAL REPORT
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CONTRACT CPA 70-66
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Office of Air Programs
Control Systems Division

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ACKNOWLEDGMENTS

Research was performed by the Coal Research Bureau, School of Mines, West Virginia University under contract with th~ Office of Air Programs--Environmental Protection Agency. The principal investigator and project director for this contract is Mr. Joseph W. Leonard, Director, Coal Research Bureau and the project officer is Mr. Luis Garcia of the Control Systems Division, Environmental Protection Agency. The authors of this report are Messrs. William Lawrence, Richard Muter, Ronald Anderson and Mrs. Linda Condry.

Appreciation is due to Mr. Charles F. Cockrell, former Assistant Director of Research of the Coal Research Bureau, for initiating and directing the contract research and to Messrs. Benedict St. Jermaine, Jr., Edward Simcoe, Jr., and Gerald Moore, lab technicians, for performing the many necessary experimental procedures.

INTRODUCTION

The increasing waste disposal problem associated with coal combustion may be compounded several fold by the greater amount of waste generated if potential alkaline earth sulfur dioxide abatement systems are implemented. Although utilization schemes for normal flyash are available, the modified flyash resulting from limestone/dolomite wet and dry sulfur sorption programs represents a new type of solid waste material having different chemical and physical properties from regular flyash. In addition, simple disposal of this ash by land fill or lagooning may result in serious water or solid waste pollution problems. Previous research[1-1, 1-2] has shown that very little potential exists for mineral separation and beneficiation of this new ash and indicates that the most economical utilization scheme would involve total utilization of the ash. For these reasons the Coal Research Bureau of West Virginia University has been performing basic research under a cost sharing grant from EPA (Environmental Protection Agency) to develop and evaluate total utilization processes. As a result of this research, several promising ash utilization schemes have emerged. These include: production of autoclaved structural materials such as calcium-silicate brick, concrete and aerated concrete; production of high temperature materials such as mineral wool; and use of modified ash as an agricultural soil amendment.

1. CHARACTERIZATION

Characterization of modified flyash was a continuation and expansion of studies initiated under Contracts PH 86-67-122[1-1] and PH 22-68-18.[1-2] The general objectives were to determine the physical and chemical characteristics of modified ashes and to monitor variability of the ash samples produced from several different magnesium oxide and calcium oxide based processes for the adsorption of sulfur dioxide. The modified flyash samples were examined by means of atomic absorption and atomic emission spectrophotometry, wet chemical analysis, microscopic analysis, wet and dry-sieve techniques and x-ray diffraction. Because the genesis of the ashes involved is a most important factor in analyzing characterization data, a detailed description of the sources of the seven different modified ashes studied is included.

A. Sources of Modified Ash

1. Detroit Edison Company, St. Clair, Michigan (PID and DW)

The project undertaken at the St. Clair, Michigan Power Station was a joint effort by Detroit Edison Company and Combustion Engineering, Inc. to field test the limestone/dolomite injection, dry- and wet-collection, sulfur oxide removal system under development by Combustion Engineering, Inc. In these tests, a small stream of the dust-laden stack gases were diverted to a wet scrubber so that both wet- and dry-collected modified flyashes were available. When the dolomite tests were completed, a high purity limestone was also injected into the boiler. Thus, it was possible to obtain both wet- and dry-collected limestone and dolomite modified flyashes from this test series. PID is a sample of the limestone modified material collected by a combination of electrostatic and mechcanical precipitators rated to be 99.5% effective and DW is dolomite modified wet-collected ash obtained from the settling tank of a wet-scrubbing circuit.

In these tests the coal (3% sulfur--Ohio strip coal) and stone were pulverized to approximately 95 percent passing 200 mesh. The crushed stone was injected through the top burner, oriented 30° above the horizontal, of a 325 megawatt Combustion Engineering twin furnace unit at a rate of approximately 10 tons per hour (180 percent of the stoichiometric sulfur gas absorbent requirement.

2. Union Electric Company, St. Louis, Missouri (SLD)

Samples of wet-collected dolomite modified flyash were obtained from the Merrimac Plant of Union Electric at St. Louis, Missouri. A dry injection wet-collection technique was employed; the coal used contained 3% sulfur. When the samples were taken, one of the two scrubbers was shut down for modification; but, the water requirement was not reduced. Dolomite of approximately 85 percent passing a 200 mesh sieve was added at the rate of 60 percent stoichiometric to the 2000°F temperature zone of the furnace. Approximately 3,000 gallons per minute of water were used; 90 percent of the water could be recycled from a clarification system. The slurry concentration of the SLD material was about two percent solids.

3. Chevrolet Motor Division Plant, St. Louis, Missouri, (CM, CI and CU)

The injection tests undertaken by Chevrolet Motor Division at their St. Louis assembly plant were performed in a small Babcock and Wilcox boiler having a capacity of two tons of coal per hour. Pre-ground commercially available dolomite was tested both by intermixing with the coal and by injection above the flame envelope.

CM modified flyash was produced by pre-mixing dolomite and coal before combustion while the CI material was produced by injecting the material above the flame envelope. CU is unmodified flyash from the same unit.

In these tests, the dolomite, vended as "dolcito,"* was injected into the boiler at a rate of 200 percent of the stoichiometric amount required. The dolomite had been pulverized by the supplier to 76 percent passing 230 mesh and 4.4 percent passing 325 mesh. The coal burned during the tests contained 3 1/2 percent sulfur and was obtained from the River King No. 2 Mine of Peabody Coal Company and the Sparta Mine of Bell and Zoller Company. The coal was fed into a B & W Type E pulverizer in a ratio of 60 percent River King to 40 percent Sparta where it was pulverized to 70 percent passing 200 mesh prior to combustion. The dry, modified flyash was collected in an electrostatic precipitator rated to be approximately 99 percent efficient.

In the initial test, dolomite was admixed with the coal by adding 50 pounds of dolomite every three minutes through the exit port of the weigh feeder. A 45 minute delay occurred between the time dolomite was first added and a stable 20% reduction of sulfur dioxide occurred. After the stable reduction occurred, the test was continued for three hours.

In the second test, dolomite was injected from a spider system specifically designed to permit the dolomite to be uniformly sprayed, via six nozzles, into the boiler above the flame envelope at an angle of approximately 45 degrees above the horizontal. This test was also of three hours duration; however, a 30% reduction of sulfur dioxide in the stack gases occurred almost immediately.

4. Kansas Power and Light Company, Lawrence, Kansas (KPL)

The tests undertaken at Lawrence, Kansas were a joint effort by the Kansas Power and Light Company and Combustion Engineering, Inc. on a full-scale, permanent wet scrubbing installation. The system used dry injection, wet-collection in which limestone, ground to approximately 60 percent

*Use of trade names does not imply endorsement by the Coal Research Bureau but is intended for clarification purposes only.

passing 200 mesh, was injected at the rate of 110 percent stoichiometric into the 2100°F temperature zone of the furnace. Two separate scrubbing units were incorporated, both of which employed an over-bed recycle system whereby water and modified ash from the bottom of the scrubber were passed to a delay and mixing tank and then recycled by being sprayed above the marble bed in the scrubber. The system used about 3,000 gallons of water per minute of which 700 gallons per minute were obtained from blow down of the cooling tower. The remaining water came from a recycle pond adjacent to the settling pond. Sulfur dioxide in the stack gases was monitored both before and after the scrubber. The coal being burned contained 1,960 parts per million (ppm) sulfur as sulfur dioxide and 760 ppm was sorbed by calcined stone in the dry state. The remaining 1,200 ppm entered the scrubber and 400 ppm were emitted to the atmosphere after scrubbing.

5. Shawnee Steam Plant, Paducah, Kentucky (TVA)

The tests performed at Paducah, Kentucky were a project of the Tennessee Valley Authority at their Shawnee Steam Plant. A limestone injection, dry-collection method was used.

High purity limestone was injected into the boiler and the resulting modified ash was collected in three different precipitators. The ash and off-gases were first passed through a mechanical precipitator and then cycled through two electrostatic precipitators before the effluent gas was fed to the stacks. Sample TVA is a sample of the flyash collected in the mechanical precipitator.

B. Chemical and Physical Analyses

Chemical analyses and physical properties of all the modified flyashes examined under the subject contract are given in Table 1-1. The chemical analyses were performed by wet chemical, atomic absorption and atomic emission spectroscopic methods; the physical properties were determined in the normal manner. The analysis of a sample of unmodified flyas.. (sample CU) is also incorporated in the table for comparison purposes.

TABLE 1-1

CHEMICAL AND PHYSICAL ANALYSES OF ASHES STUDIED

Identification Name	PID	DW	SLD	CM	CI	CU	KPL	TVA
Source	Detroit Edison	Detroit Edison	Union Electric	Chevrolet St. Louis	Chevrolet St. Louis	Chevrolet St. Louis	Kansas Power and Light	TV. Ey
Modifying Stone	Limestone	Dolomite	Dolomite	Premixed Dolomite	Injected Dolomite	Unmodified	Limestone	Limestone
Mode of Collection	Dry	Wet	Wet	Dry	Dry	--------	Wet	Dry
CHEMICAL PROPERTIES (%)								
SiO_2	30.85	23.34	30.80	35.90	33.10	48.40	29.90	32.60
Al_2O_3	13.70	9.03	14.70	14.40	11.80	18.40	8.42	16.70
Fe_2O_3	11.59	9.99	7.01	7.76	7.18	13.60	12.40	4.28
TiO_2	0.68	0.43	0.64	0.71	0.65	1.10	0.40	0.56
CaO	29.79	13.84	19.56	19.18	17.92	5.18	28.60	36.80
"free" lime	-----	-----	-----	8.96	7.70	0.00	6.05	24.69
MgO	1.49	9.24	4.77	12.61	11.45	1.66	2.14	0.54
Na_2O	1.12	0.65	0.36	0.34	0.46	0.58	0.23	5.05
K_2O	0.71	0.83	1.42	0.72	0.72	1.30	1.29	0.92
SO_3	2.20	18.68	15.33	8.05	6.95	3.18	12.93	2.65
C	1.12	2.11	1.49	3.29	5.64	9.67	1.22	3.36
Moisture	0.00	slurry	98.00	0.24	0.26	0.30	97.70	0.03
Loss on Ignition	1.03	9.00	6.13	3.79	8.34	11.58	10.00	9.08
Water Soluble Fraction	22.11	21.08	25.50	25.61	19.14	8.90	20.24	6.94
PHYSICAL MELTING PROPERTIES (°F)								
Initial Deformation Temperature	2071	2061	1780	1870	1720	1890	1620	2010
Softening Temperature (Spherical)	2138	2237	2140	2260	2250	2250	2140	2180
Softening Temperature (Hemispherical)	2145	2246	2150	2270	2270	2260	2150	2190
Fluid Temperature	2172	2260	2160	2300	2280	2270	2165	2180

As shown in Table 1-1, relatively large amounts of calcium, reported as the oxide, were present in all of the modified ashes. Also, as would be expected, samples of dolomite modified ashes contained a higher percentage of magnesium oxide. Although the difference in chemical composition could be explained by a simple dilution effect of the alkaline earths on normal flyash, modified ash should be considered a "new-ash" material. The uniqueness of modified flyash is best characterized by the physical properties of the material. Fusion characteristics, as indicated in Table 1-1, show that initial deformation and melting occur at significantly lower temperatures than for normal flyash. Mineral wool testing, employing a mixture of normal flyash and equivalent amounts of lime as in the modified ash, demonstrated that the viscosity of molten modified flyash at a specific temperature was lower than that of a normal flyash-lime mix. Further evidence of the uniqueness of modified flyash is supplied by the fact that due to the high resistivity of modified flyash the efficiency of electrostatic precipitators drops markedly when alkaline earth injection is used.[1-4]

Using a modification of the Moorehead and Taylor method for calcium oxide determination,[1-5] "free" lime determinations were performed to measure the amounts of unreacted calcium oxide (CaO) and calcium hydroxide [$Ca(OH)_2$] present in the modified ash samples. This "free" lime is capable of mixing with the inherent pozzolanic portions of flyash to form natural cementitious materials. The greater the amount of "free" lime present in a modified ash, the greater are the potential cementitious properties of the ash.

C. Sieve Analyses

Particle size analyses using both dry- and wet-sieve methods were performed on three modified ashes--limestone injected wet-collected KPL, limestone injected dry-collected TVA and dolomite mixed dry-collected CM. In this analysis, dry-collected ashes were dry sieved and KPL was wet sieved. These tests were performed to determine the size distribution of the ashes and to

provide necessary data for possible beneficiation processes. The size distributions of the three ashes are:

	WEIGHT PERCENT OF TOTAL FRACTION		
U. S. S. Sieve	KPL	TVA	CM
+60 mesh	0.6	0.1	0.0
60 x 200 mesh	2.3	33.6	4.6
200 x 325 mesh	5.9	25.6	36.6
325 x 400 mesh	6.5	18.8	56.2
-400 mesh	84.7	21.7	2.6

KPL and CM contain large amounts of fine particles (over 95%, -200 mesh) which is due, in part, to the mode of collection. Sample KPL was collected by a wet-scrubbing system; sample CM was collected by an electrostatic precipitator. On the other hand, TVA modified flyash was collected by a mechanical hopper which is not as effective for trapping very fine particles as the other methods. Hence, TVA had the coarsest particle size distribution of the three samples.

The chemical analysis of each sieve fraction can be found in Table 1-2. The results are reported as percent of the total compound present in the head sample. As can be seen from the table, little or no beneficiation of the elements listed were attained through sieve methods.

D. Microscopic Analyses

Microscopic analyses were performed on wet-collected samples from the Kansas Power and Light Company (KPL) and from Union Electric of St. Louis (SLD). Samples were dried and examined under magnification (50x, 500x, 900x) and appeared to be very similar to the samples of PID, dry-collected limestone modified flyash, previously studied.[1-2]

KPL was then separated, using the sink-float technique employed on PID, into specific gravity fractions ranging from 2.00 to 2.96 SG. The most visually distinct separation was observed when using a medium of 2.20 SG. The float portion was gray in color while the sink was black. Microscopic observation indicated that the float fraction consisted of approximately equal amounts of white or yellow, irregulary shaped particles and irregular

TABLE 1-2

CHEMICAL ANALYSIS OF MODIFIED ASH FRACTIONS

Chemical Analysis
(% of Total Amount Present in Head Sample)

Sample	Size Fractions (USS Mesh)	Weight % of Total Fraction	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO
	Head Sample	100.0	29.9	8.4	12.4	0.4	28.6	2.1
	+60	0.6	0.3	0.0	0.3	0.4	0.9	0.6
	60 x 200	2.3	3.0	2.3	2.2	2.0	2.0	2.3
	200 x 325	5.9	8.2	7.0	6.3	6.1	5.3	6.5
KPL	325 x 400	6.5	8.0	6.8	8.3	6.9	4.4	7.4
(wet-sieved)	-400	84.7	80.5	83.9	82.9	84.7	87.4	83.2
	Head Sample	100.0	35.9	14.4	7.8	0.7	19.2	12.6
	+60	0.0	----	----	----	----	----	----
	60 x 200	4.6	5.1	5.6	3.0	5.0	1.9	4.4
	200 x 325	36.6	37.6	42.2	20.5	34.7	54.3	37.3
CM	325 x 400	56.2	54.7	49.4	73.4	57.7	41.7	88.7
(dry-sieved)	-400	2.6	2.6	2.9	3.1	2.6	2.1	3.2
	Head Sample	100.0	32.6	16.7	4.3	0.6	36.8	0.5
	+60	0.1	0.0	0.0	0.0	0.1	0.2	0.1
	60 x 200	33.6	31.2	27.8	16.0	25.7	42.8	34.0
	200 x 325	25.6	24.3	26.0	28.4	24.9	23.8	23.5
TVA	325 x 400	16.3	20.3	21.6	23.7	21.4	17.9	19.8
(dry-sieved)	-400	21.7	24.2	24.5	31.3	27.9	15.4	22.8

black particles. The light colored irregular particles, when hand crushed, broke into clear hollow spheres, clear solid spheres which were siliceous in nature and a very fine white powder--calcium constituents. It appeared that this white powder coats the spheres and binds them together to form the larger irregular particles. The sink portion was composed of black spherical particles with a few scattered irregular white ones. When the black particles were hand crushed, it was observed that they consisted of ferruginous shells over white spheres which appeared to be siliceous in nature. Thus, it was found that this wet-collected modified flyash was physically very similar to the dry-collected material previously tested.

In order to further study the binding of the lighter colored particles, a head sample of KPL was leached with hydrochloric acid and examined under the microscope. It was noted that after leaching very little of the bonding material evident before leaching remained. The leached sample was filtered, dried and observed again under the microscope. It was evident that the particles consisted of distinct white spheres and irregular black shapes. The leached sample was then submitted for chemical analysis by emission spectroscopy. The analysis showed a reduction in CaO from 27.13 to 21.91 in the leached portions. Thus, it appears that the particle binding may be attributed to the calcium constituents of sample KPL.

Flyash sample SLD was also examined using the same methods. The results were very similar to those reported for flyash KPL except that the sharpest visual color separation occurred at a specific gravity of 2.30. The float material was slightly darker to the eye than the float of KPL and upon microscopic observation was seen to contain a higher percentage of irregular black particles.

E. X-ray Analyses

To further characterize modified flyash, samples were submitted for x-ray analysis. Diffraction patterns were obtained but could not be analyzed as interpretive difficulties were encountered due to the massive number of diffraction lines detected and to inconsistent results obtained using an ASTM program for computer-assisted data reduction. The three most probable explanations of this are 1) that modified flyash contains a high percentage of low-ordered structures which produce random scattering and do not yield distinct patterns which can be resolved; 2) that the high heats involved in the coal-limestone combustion process produce high-temperature, metastable structures which cannot be analyzed by diffraction methods; (These high heats also thermally damage known compounds so that even those compounds whose diffraction patterns can be found in ASTM specifications would be very difficult to analyze) and 3) that a more complete chemical analysis of modified ash is needed. This analysis must determine the presence of not only the main constituents of the ash (such as calcium or silicon), but also trace elements and anion constituents so that more information could be made available. This added information would make the computer program more reliable.

Concurring with other research[1-6] we must conclude that due to the many low-ordered structures and the few crystalline materials present in modified flyash, great difficulty is experienced in interpreting x-ray diffraction pattern of modified flyash. This difficulty is encountered because x-ray diffraction results are almost entirely dependent on the presence of crystalline material. Therefore, if a molecular analysis of modified ash is considered desirable, other methods of investigation should be employed.

F. Summary

The main constituents of modified flyash are silicon, calcium (and magnesium if dolomite is used as the modifying stone), aluminum, iron and sulfur. Wet-collected modified ashes usually have a higher sulfur content than dry-collected ashes though the amount of sulfur present in the ash is determined not only by the efficacy of the collection system but also by the amount of sulfur found in the coal used. The physical melting properties of modified flyashes are quite similar and all ashes tested melted within a temperature range of 2150-2300°F. This similarity of physical characteristics is further substantiated by microscopic analysis. Modified flyash is normally a powder-like material of small particle size. Predominant size fractions of almost all ashes tested were 325 x 400 or -400 mesh. Sieve analysis of the three ashes most often used in this contract showed little or no beneficiation of elements upon sieving.

Characterization

1-1 Cockrell, C. F., Muter, R. B., and Leonard, J. W., "Study of the Potential for Profitable Utilization of Pulverized Coal Flyash Modified by the Addition of Limestone-Dolomite Sulfur Dioxide Removal Additives," Final Report, Contract PH 86-67-122, National Air Pollution Control Administration, April, 1969.

1-2 Anderson, Ronald E., Cockrell, Charles F., et al., "Study of Potential for Recovering Unreacted Lime from Limestone Modified Flyash by Agglomerate Flotation," Final Report, Contract PH 22-68-18, National Air Pollution Control Administration, May, 19770.

1-3 Personal Communication, David T. Clay, Air Pollution Control Office--Resident Engineer, Shawnee Steam Plant, Paducah, Kentucky. April 20, 1971.

1-4 Walker, A. B. and Brown, R. F., "Effects of Boiler Flue Gas Desulfurization Dry Additives on the Design of Particulate Emission Control Systems," Paper presented at the Dry-Limestone Injection Process Symposium, National Air Pollution Control Administration. Gilbertsville, Kentucky, June 22-26, 1970.

1-5 Moorehead, D. R. and Taylor, W. H., "Sucrose Extraction Method of Determining Available CaO in Hydrated Lime," ASTM Bulletin. No. 236, 1967, pp 45-47.

1-6 Minnick, L. John, "Reactions of Hydrated Lime with Pulverized Coal Fly Ash," USBM Information Circular 8348: Fly Ash Utilization. 1967, p 312.

2. CALCIUM-SILICATE STRUCTURAL PRODUCTS

Because modified flyash liberates sorbed sulfur dioxide at elevated temperatures (between 1700 and 2200°F), it is necessary to find a total utilization method which would either lock the sulfur into a product or which would require no large external application of heat. Preliminary research investigating the natural pozzolanic activity of limestone modified flyash indicated that some cementitious setting occurred. Such setting is sufficient to obstruct power plant process lines if water flow should stop, but does not appear to impart enough strength for structural products. In an effort to increase pozzolanic activity and consequently strength characteristics and since the technology has been well developed in Europe using normal flyash, autoclaved calcium-silicate (CS) building materials were examined as a potential use for modified ash.

The most common types of CS structural products are brick, concrete and aerated or foamed cellular concrete. The primary difference between CS brick and common American products such as cement block or concrete block is that the CS brick are autoclaved instead of air or steam cured. Autoclaving produces the desired tobermorite ($5CaO \cdot 6SiO_2 \cdot 5H_2O \cdot 6CaO \cdot 6SiO_2 \cdot 5H_2O$) type cement binding in a span of hours rather than the days or months needed to cure cement or concrete block. Thus, strength and final dimensions are acquired during the manufacturing process and large curing storage areas are not required. In addition, the production of CS-type structural products has two major advantages as a utilization process for modified flyashes. These are:

1. There are no sulfur gas capture or marketing problems. All processing occurs below the temperatures necessary for sulfur dioxide regeneration; and

2. There have been no pollution problems from soluble sulfur noted, as the sulfur components of modified flyash are combined chemically and are bound within the matrix structure of the autoclaved product.

A. Calcium-Silicate Bricks

Calcium-silicate bricks of superior quality (compressive strengths in excess of 7000 psi) were produced from limestone and dolomite modified flyashes through the process illustrated in the accompanying flowsheets, Figures 2-0 and 2-1. Experimental work proceeded in three phases with pellets (1" diameter by 3/8" thickness) being made initially to determine basic composition mixtures, forming pressures and autoclaving conditions for each individual modified flyash examined. Samples CM*, dry-collected modified ash, and KPL*, wet-collected ash, were selected for the second phase of research--the production of 2" x 4" x 1 3/8" bench-scale brick--as they were the only ashes of their types available in sufficient quantity. This phase of the research dealt primarily with such processing variables as forming pressure, mixing, humidity curing, etc. In the final phase, full size brick were produced using common commercial equipment to determine whether, in actuality, the process could be scaled up.

Data obtained from the pellet tests indicated that CS brick could be produced from modified flyash. When using dry-collected modified flyash, the brick mix consisted of 50% (on a dry basis) modified flyash, 50% silica sand and approximately 20% water (see Figure 2-0); when wet-collected modified flyash was used, CS brick could be produced containing 50% (on a dry basis) modified flyash, 39% sand and 11% calcium oxide (see Figure 2-1). Using wet-collected KPL flyash, the process involved a dewatering of the slurry to 34% water before mixing. Such a composition provides sufficient water for mixing and forming of the green brick.

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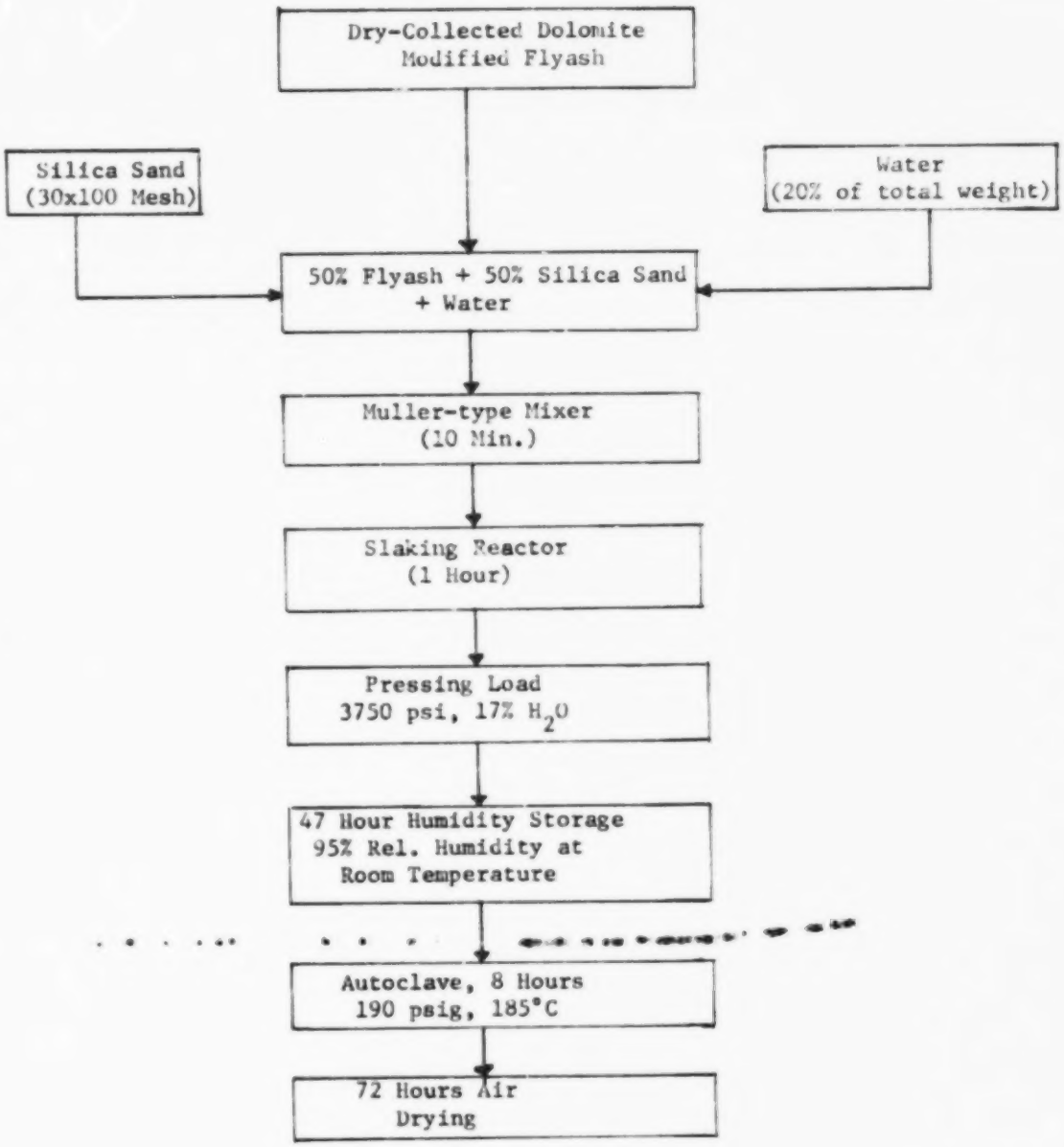
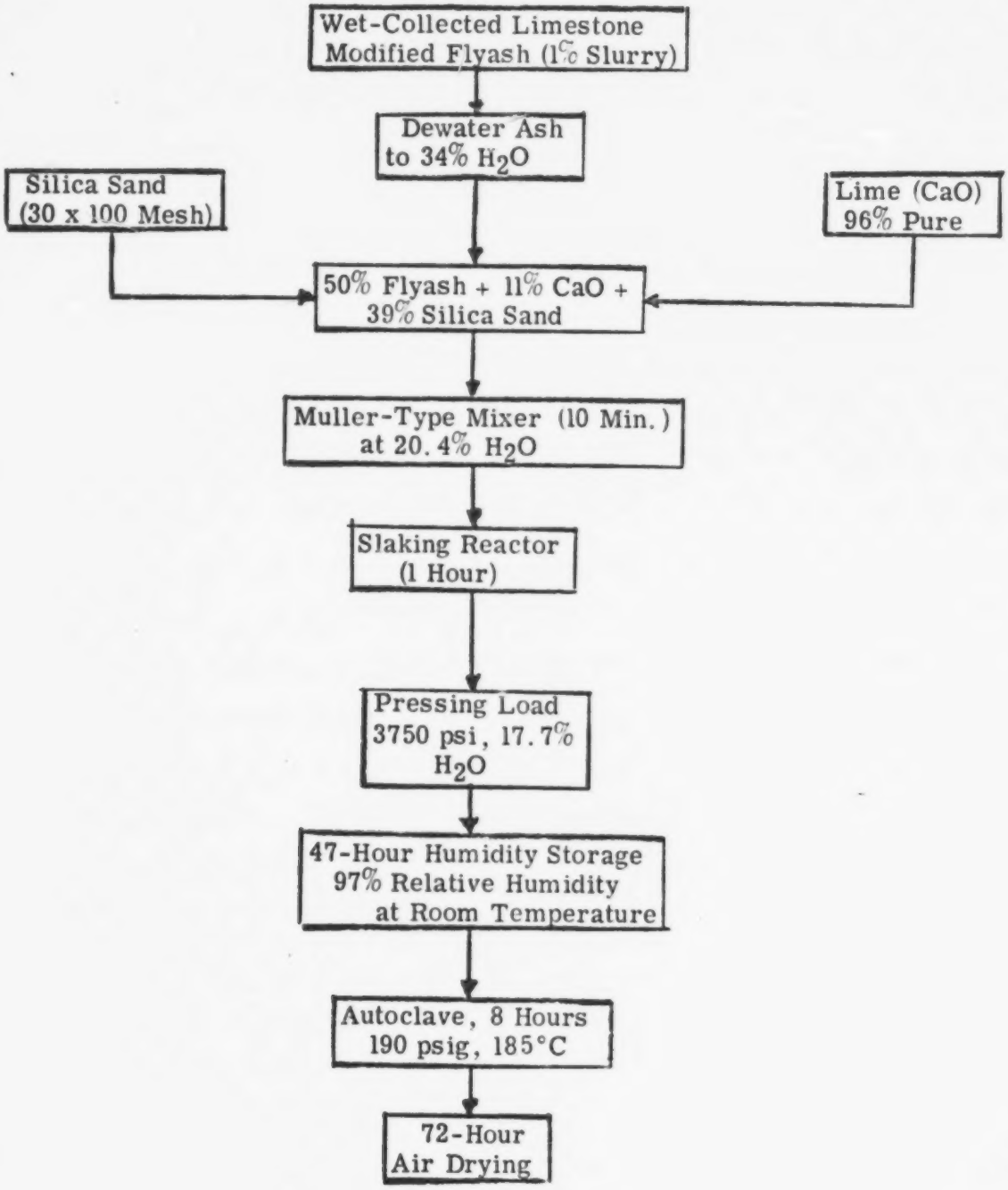
*These ashes are described in detail in the Characterization Section of this report.

Figure 2-6


Dry-Collected Dolomite Modified Flyash
Silica Sand (30x100 Mesh)
Water (20% of total weight)
50% Flyash + 50% Silica Sand + Water
Muller-type Mixer (10 Min.)
Slaking Reactor (1 Hour)
Pressing Load 3750 psi, 17% H_2O
47 Hour Humidity Storage 95% Rel. Humidity at Room Temperature
Autoclave, 8 Hours 190 psig, 185°C
72 Hours Air Drying

Flow Sheet: Optimum Conditions for the Production of Calcium-Silicate Brick from Dry-Collected Modified Flyash.

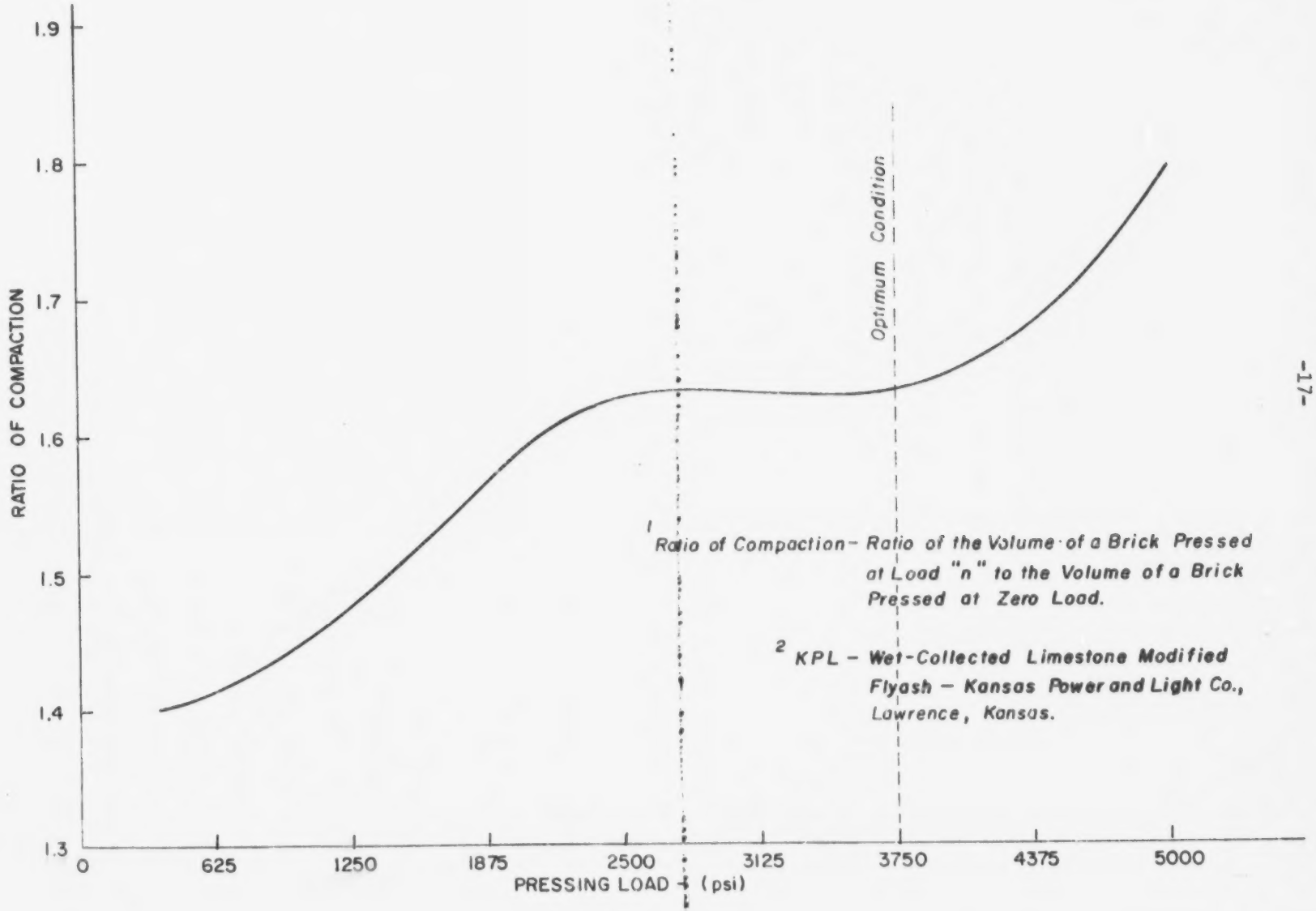
Figure 2-1


Wet-Collected Limestone Modified Flyash (1% Slurry)
Dewater Ash to 34% H_2O
Silica Sand (30 x 100 Mesh)
Lime (CaO) 96% Pure
50% Flyash + 11% CaO + 39% Silica Sand
Muller-Type Mixer (10 Min.) at 20.4% H_2O
Slaking Reactor (1 Hour)
Pressing Load 3750 psi, 17.7% H_2O
47-Hour Humidity Storage 97% Relative Humidity at Room Temperature
Autoclave, 8 Hours 190 psig, 185°C
72-Hour Air Drying

Flow Sheet: Optimum Conditions for the Production of Calcium Silicate Brick from Wet-Collected Modified Ash

FIGURE 2-2

THE RELATIONSHIP OF THE RATIO OF COMPACTION[1] AND PRESSING LOAD FOR KPL[2] BRICK MIX

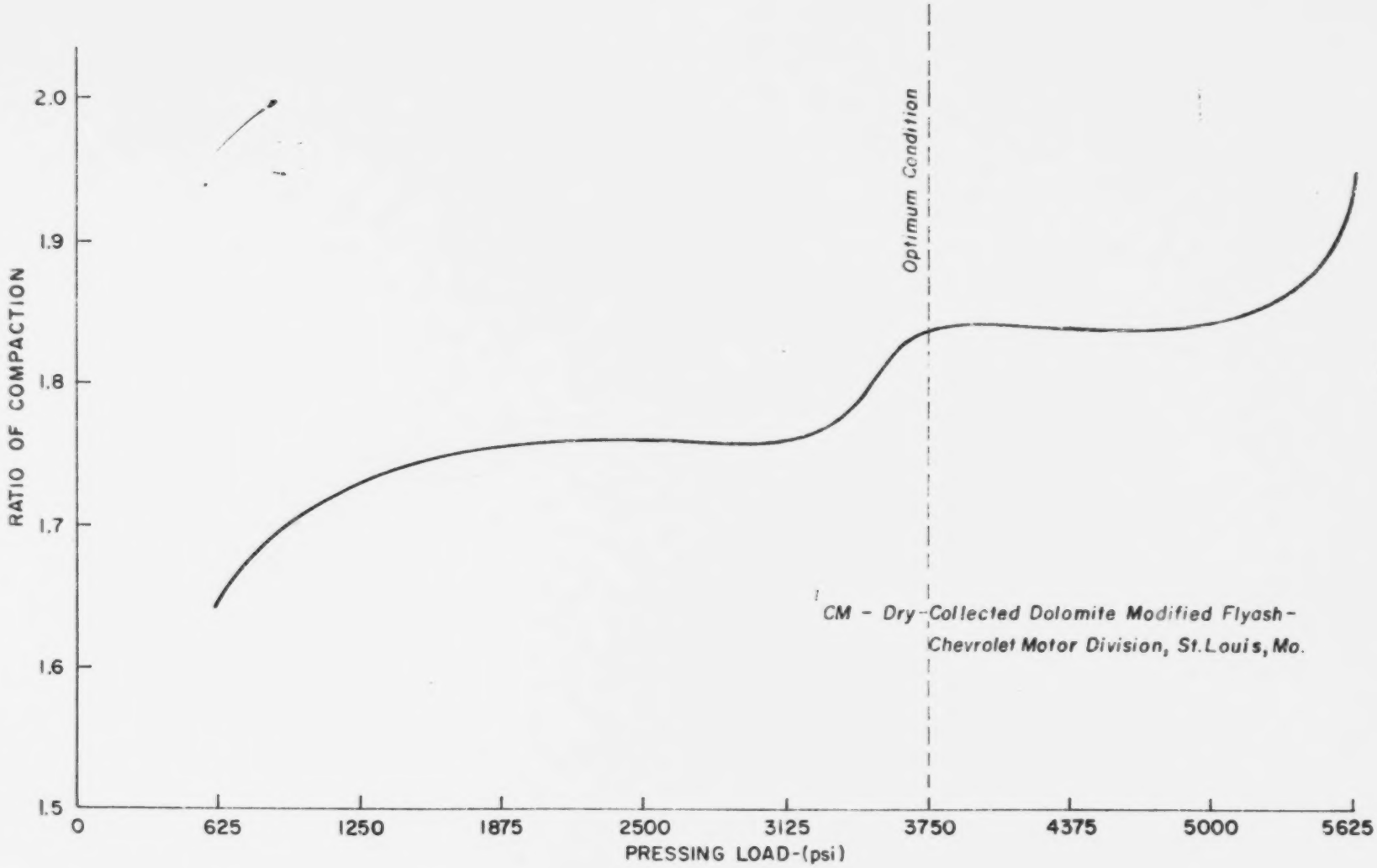


[1] Ratio of Compaction – Ratio of the Volume of a Brick Pressed at Load "n" to the Volume of a Brick Pressed at Zero Load.

[2] KPL – Wet-Collected Limestone Modified Flyash – Kansas Power and Light Co., Lawrence, Kansas.

FIGURE 2-2a

THE RELATIONSHIP OF THE RATIO OF COMPACTION AND PRESSING LOAD FOR CM[1] BRICK MIX



[1] CM - Dry-Collected Dolomite Modified Flyash - Chevrolet Motor Division, St. Louis, Mo.

FIGURE 2-3

THE RELATIONSHIP OF PRESSING LOAD TO PERCENT ABSORPTION AND TO COMPRESSIVE STRENGTH IN KPL BRICK

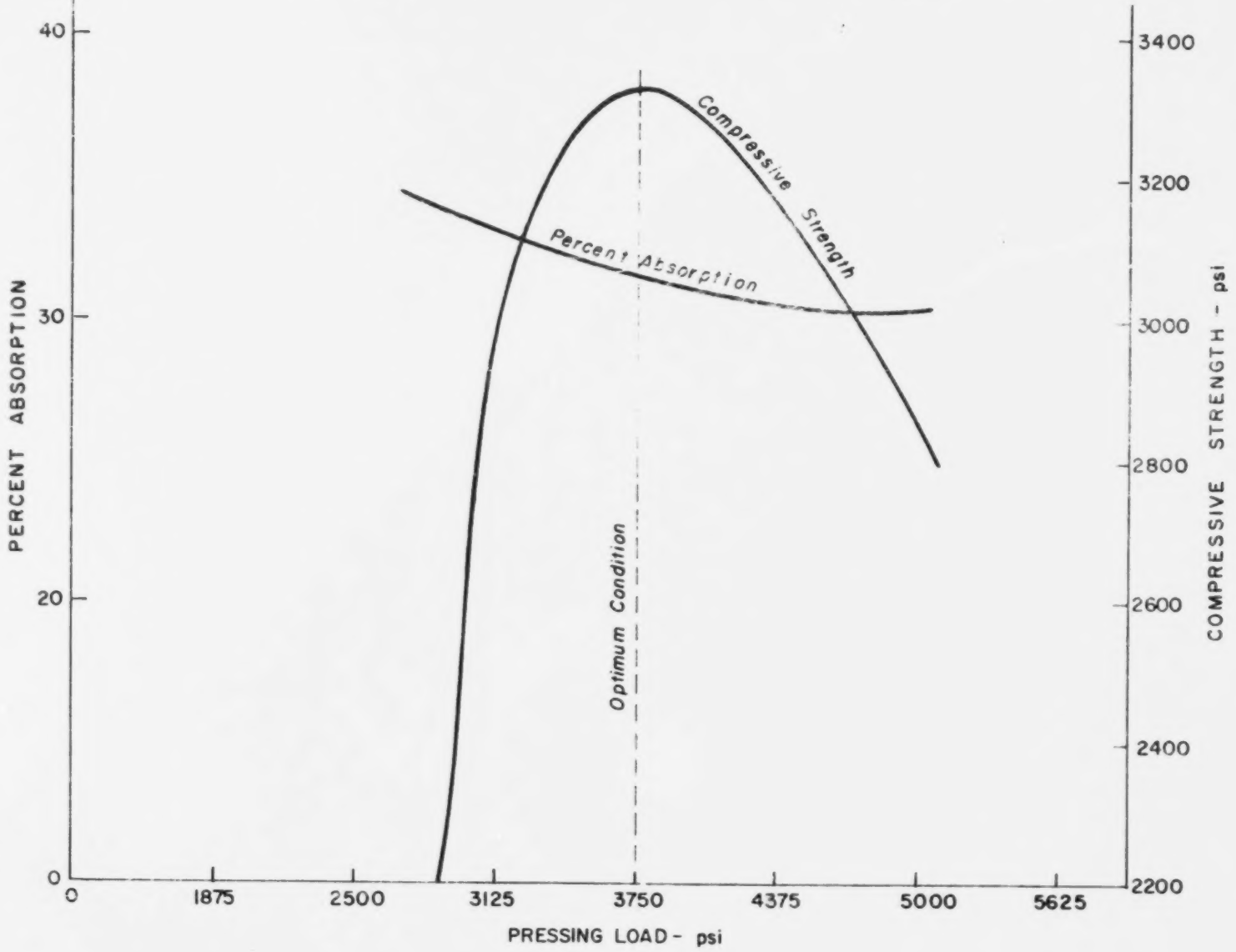


FIGURE 2-4

THE RELATIONSHIP OF HUMIDITY STORAGE TIME TO COMPRESSIVE STRENGTH AND TO PERCENT ABSORPTION IN KPL BRICK

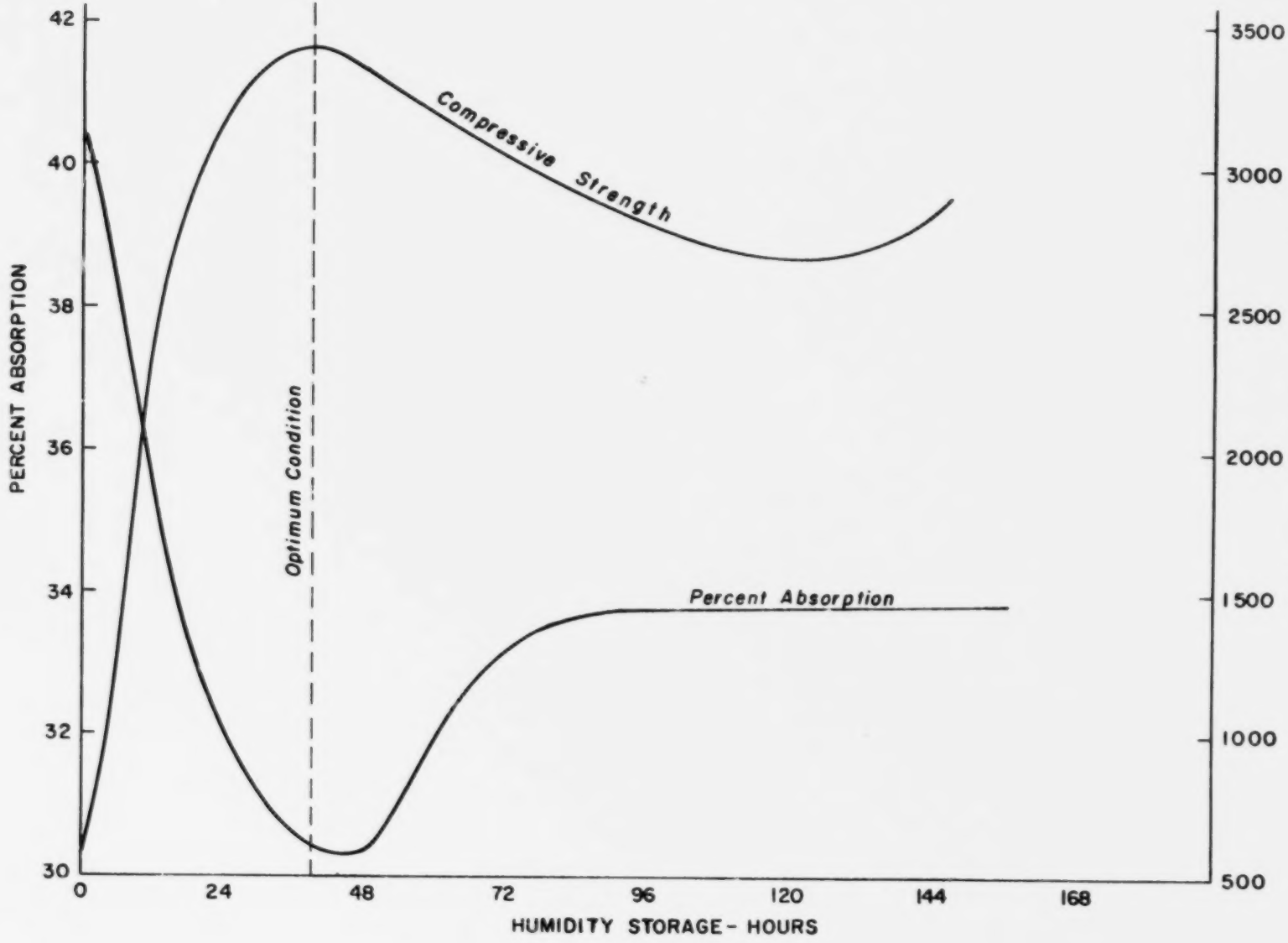
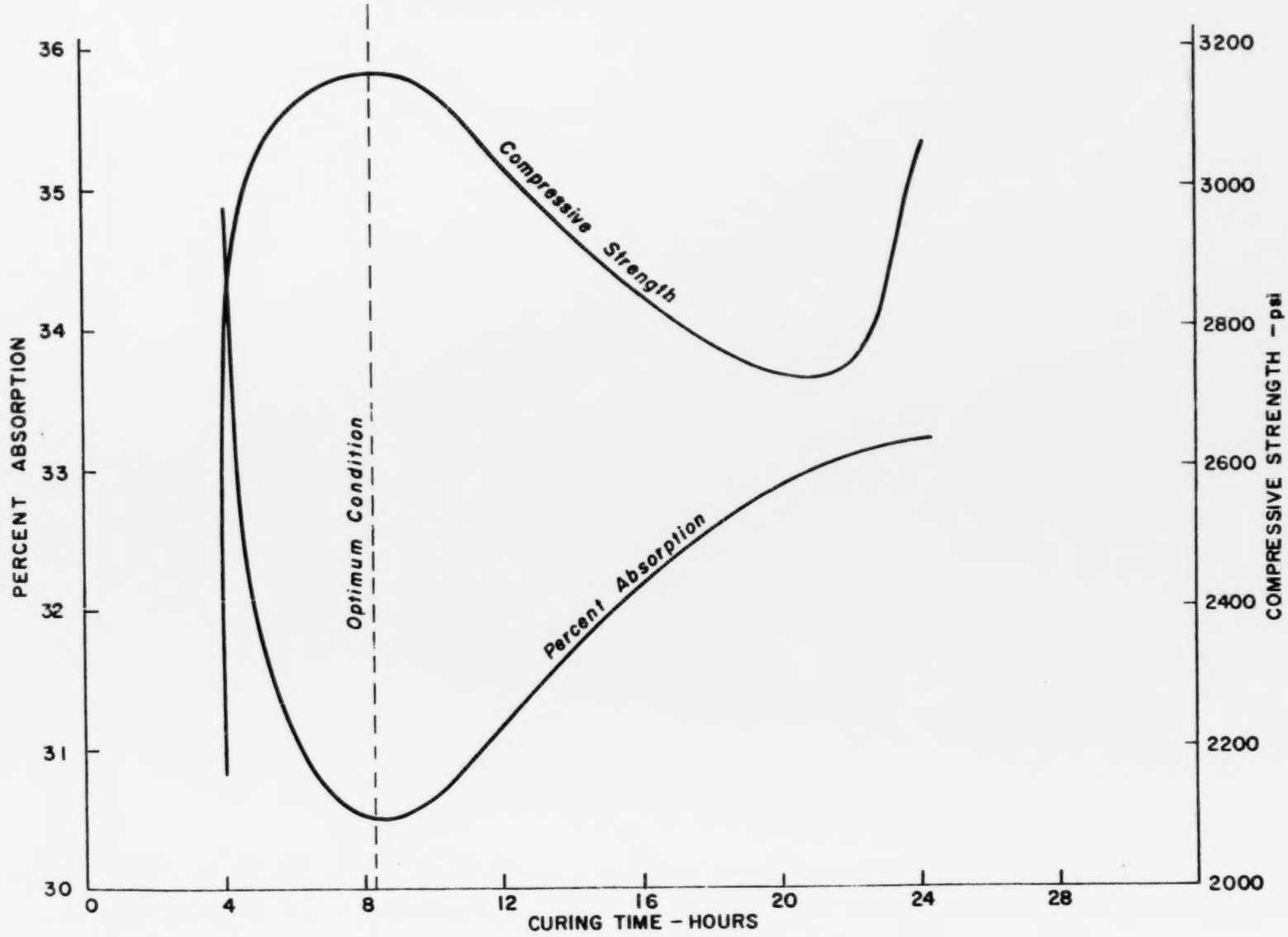


FIGURE 2-5

THE RELATIONSHIP OF CURING TIME TO COMPRESSIVE STRENGTH
AND TO PERCENT ABSORPTION IN KPL BRICK



Ratio of compaction diagrams included as Figures 2-2 and 2-2a, were prepared for CM and KPL brick mixes to aid in the determination of optimum pressing loads. Figures 2-3 through 2-5 illustrate how other process factors for the production of brick from KPL were optimized. In addition to such factors as pressing load, humidity curing time and autoclaving time shown in these figures, it was noted that intimate mixing is a necessity. A muller-type mixer proved satisfactory for this step.

In the final phase of the testing program, 2" x 4" x 8" full size brick samples were prepared using a hydraulic-toggle dry-press. The final products met or surpassed ASTM (73-51 and 73-67) specifications of 4500 psi compressive strengths and less than 1% shrinkage for grade SW, severe weathering, calcium-silicate brick. An average batch of brick made from dry-collected ash displayed characteristics of 4600 psi compressive strength, 20% absorption and no measurable shrinkage; wet-collected ash produced brick with an average 4500 psi compressive strength, 28% absorption and no measurable shrinkage. Production conditions for an optimum product can be found in Figures 2-0 and 2-1.

B. Aerated Concrete

Aerated or foamed cellular concrete is a lightweight structural material consisting of small non-communicating gas cells entrained in a calcium-silicate matrix. It is produced by inducing gas bubbles within a cementitious paste normally composed of cement and/or lime and a fine grained siliceous material.

The bubbles of gas are produced by one of two general methods:

1) By the formation of gas by chemical reaction within the mix during the liquid or plastic stage, for example:

$$2Al + 3Ca(OH)_2 + 6H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 3H_2\uparrow ;$$

or

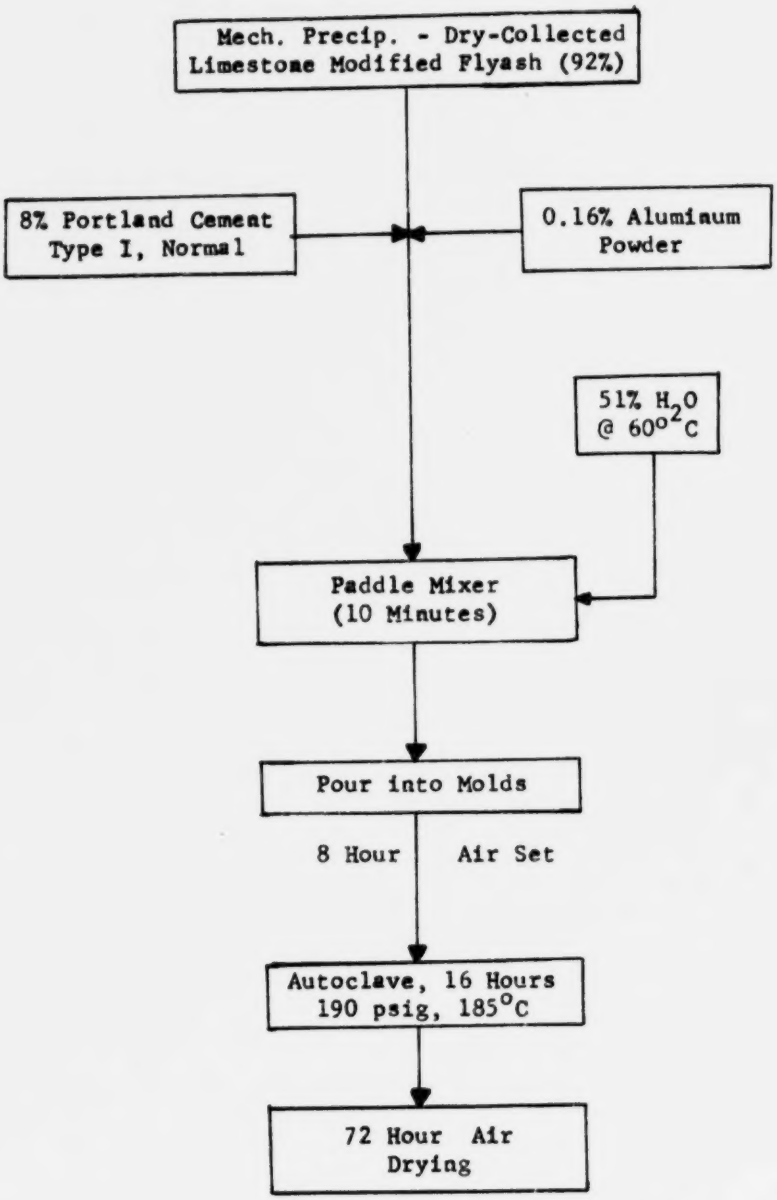
2) By introducing air from without, either by adding a preformed foam or by incorporating air by whipping.

When the first method is used, the hydrogen in the cells are replaced by air in a short time. Therefore, no fire hazard exists when foam is formed by hydrogen gas.[2-9] The gas-cement mixture is allowed to set in air and is then steam cured at high pressure. Aerated concrete made in Europe using normal coal flyash as the siliceous component is high in strength and light in weight--their best products having compressive strengths of 200-800 psi for concrete with a desntiy range of 30-45 lb/cu ft. Aerated concrete also exhibits advantageous thermal insulation and accustic properites.

Aerated concrete was produced from dry-collected limestone modified flyash using the process shown in Figure 2-6. The technology employed is essentially that used by European manufacturers with one basic exception. Utilizing the "free" lime content in dry-collected modified ash, the addition of lime is not required--a significant cost factor. Aluminum powder is used to generate gas bubbles and portland cement is added to provide strength.

Dry-collected limestone modified flyash from the Shawnee Steam Plant at Paducah, Kentucky (TVA) was selected for the bench-scale production of aerated concrete because of its high reactive or "free" lime content and its large siliceous component. It was found that aerated concrete could be prepared from this ash without the use of any additional material except water and aluminum powder--the aerating agent. The cured concrete had a compressive strength of 400 psi at a density of approximately 50 lbs/ft^3. Portland cement was then added to the mix to increase the compressive strength of the product. Although the density increased to 56.3 lbs/ft^3 when using cement, the compressive strength was increased to more than 855 psi. The addition of portland cement also stabilized the aerated mix prior to autoclaving. This is a critical factor, as setting must occur after aeration is completed and before the entrained bubbles collapse.

FIGURE 2-6


Mech. Precip. - Dry-Collected Limestone Modified Flyash (92%)
8% Portland Cement Type I, Normal
0.16% Aluminum Powder
51% H_2O @ 60^oC
Paddle Mixer (10 Minutes)
Pour into Molds
8 Hour
Air Set
Autoclave, 16 Hours 190 psig, 185^oC
72 Hour Air Drying

FLOW SHEET: AERATED CONCRETE

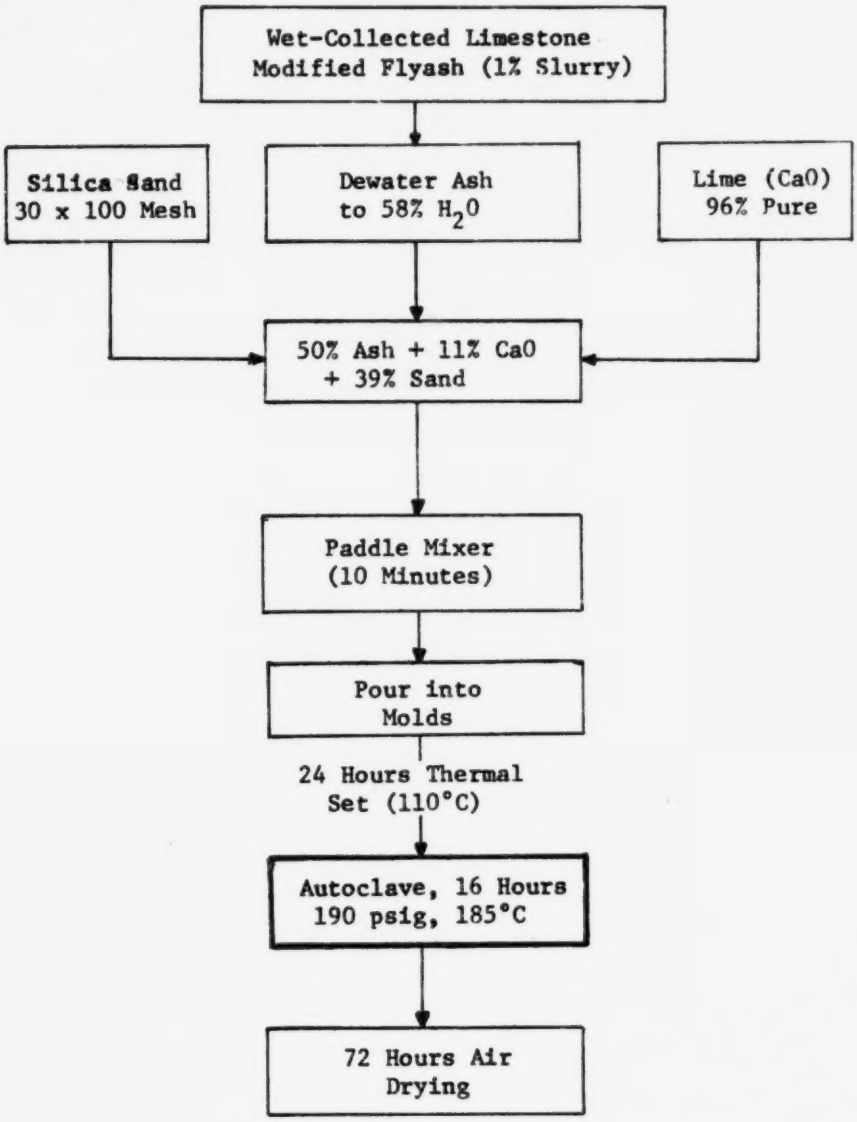
Only a preliminary investigation has been completed concerning the production of aerated concrete from modified flyash. Results of this work, however, are highly promising as the compressive strengths obtained in a few tests rivaled those found in the European product and it is felt that further study should be conducted in this area by testing other setting agents (such as $CaCl_3$ and triethanolamine) to further increase the strength and lower the density of the final product.

C. Formed Concrete Products

The natural pozzolanic properties of modified flyash indicated that a potential use might be as a cementing agent in concrete materials. Because research on CS brick production showed that autoclaving increased calcium-silicate bond formation, further research was performed to investigate the feasibility of using modified ash as the cementing agent for the production of concrete block.

Included as Figure 2-7 is the process flowsheet employed in this phase of research. It should be noted that the composition is the same as for CS brick with the exception that less dewatering is required. Also, it should be pointed out that the material is poured into molds instead of pressed. As with CS brick, this composition consisted, on a dry basis, of 50% wet-collected modified flyash, 39 percent silica sand (30 x 100 mesh) and 11 percent lime (95 percent CaO). The resulting poured concrete which is similar to concrete block had a bulk density of 90 lb/ft^3 as compared to 150 lbs/ft^3 for conventional concrete block and a compressive strength of approximtely 900 psi as compared to 1000 psi for conventional block. Although addition of the necessary aggregate could raise the bulk density to 100 lb/ft^3, this would still be only 2/3 the bulk density of standard block. Storage requirements could also be reduced as this is a full strength, non-shrinking product out of the autoclave and does not require the 3 to 4 weeks air curing time before sale as

FIGURE 2-7



FLOW SHEET: FORMED CONCRETE

does conventional concrete block. In addition, besides low cost of the raw material, an advantage of the use of modified ash is that no prior grinding or crushing of the raw material is required.

D. Conclusions

Modified flyash is an acceptable raw material for calcium-silicate building products. Brick, concrete block and aerated concrete have been produced from modified ash and display physical characteristics that approach or equal those of conventional materials. However, certain cost factors and marketing situations effect the practicality of producing calcium-silicate building materials from modified ash. The low cost of raw materials (eg, in some areas flyash sells for as little as $1 per ton) reduces the production of CS material and the reduced weight of the material decreases the handling and labor costs at final construction sites. Conversely, in the United States the production of CS building material involves new techniques of production such as autoclaving and dewatering. In addition, there exists a lack of acceptance by American industry of new building products. Therefore, even though the production of CS building material from modified ash has been shown to be an implemental flyash utilization scheme and a practical method for producing quality building products, the large capital investments involved in structuring new processing plants and the resistance of labor and the structural clay products industry in accepting new building materials appear to be an overwhelming economical deterrent to the commercial production of CS building products.

Sand-Lime Brick

2-1 Brick and Tile Construction. Structural Clay Products Institute, Washington, D. C., 1964.

2-2 Mateos, Manuel, "Heat Curing of Sand-Lime-Flyash Mixtures," Materials Research and Standards. May, 1964, pp 212-217.

2-3 Oberschmidt, Leo E., "Widespread Interest Signals The Resurgence of Sand-Lime Brick," Brick and Clay Record. Vol. 154, No. 4, April, 1969, pp 16-18.

2-4 Redecker, Immo H., "Sand-Lime Bricks," Speech delivered at the Southeastern Section American Ceramic Society, Gatlinburg, Tennessee, July 1, 1966.

2-5 Seigle, H. D., "Method of Making Bricks," U. S. Patent No. 3499069, March 3, 1970.

2-6 Society of Chemical Industry, Autoclaved Calcium Silicate Building Products. Gordon and Breach Scientific Publishers, Inc., New York, 1967.

2-7 "Standard Specifications for Calcium-Silicate Face Brick (Sand-Lime Brick)," ASTM Designation C73-67, ASTM Standards Part 12, 1968, pp 686-687.

2-8 Taylor, W. H., Concrete Technology and Practice. American Elsevier Publishing Company, New York, 1965.

2-9 PFA Data Book. Central Electricity Generating Board, England, 1969.

3. SULFUR DIOXIDE REGENERATION

The primary purpose of limestone/dolomite injection scrubbing systems is to entrap the harmful sulfur dioxide gas produced during the combustion of coal thereby resulting in cleaner effluent gases. Theoretically, the carbonate rocks are calcined by the high heats present in the boiler during combustion,

$$\text{eg, } CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow . \qquad (1)$$

The calcined lime (CaO) then reacts with the sulfur dioxide present in the stack gas to form sulfate, and some sulfite or sulfide compounds. Some possible reactions are:

$$CaO + SO_2 \longrightarrow CaSO_3; \qquad (2)$$

$$CaSO_3 + 1/2\ O_2 \longrightarrow CaSO_4; \text{ and} \qquad (3)$$

$$4CaSO_3 \longrightarrow 3CaSO_4 + CaS. \qquad (4)$$

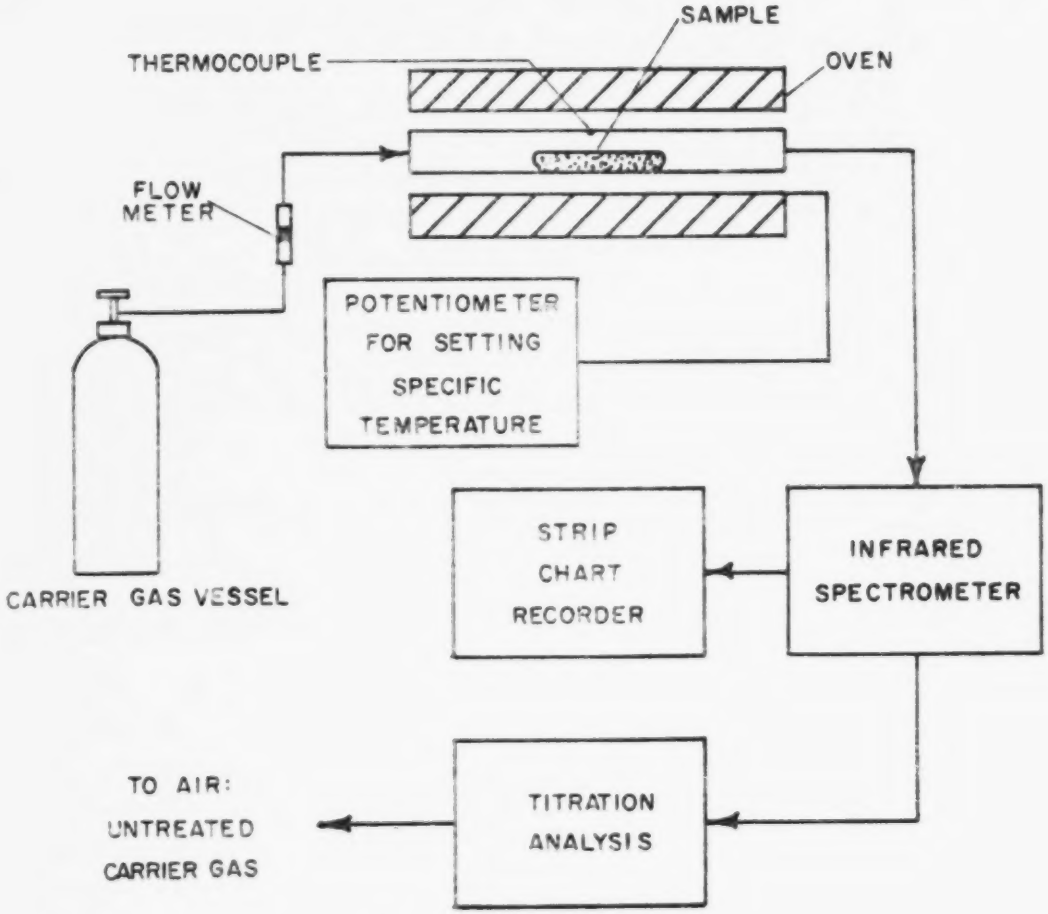
If regeneration is feasible, the high concentration of sulfur compounds present in modified ash could prove to be a practical reservoir of sulfur dioxide gas for later use by industry.

A. Experimental Method

Tests were undertaken to determine the feasibility of regenerating sulfur dioxide from modified flyash. A pre-heated tube furnace was continuously flushed with compressed air, the carrier gas, to effect an oxidizing atmosphere. Once a specific temperature was obtained, measured samples of both dry- and wet-collected modified flyash were placed in the center of the heated tube. Due to the small sample size, it was assumed that the equilibration of sample temperature to tube temperature was immediate. The effluent gases from the heating process were passed through an infrared spectrometer to identify the evolved gases. They were then passed through specific absorbing mediums (such as ascarite) to absorb any carbon dioxide or water vapor before sulfur dioxide

FIGURE 3-0

SCHEMATIC OF EXPERIMENTAL DESIGN



levels were measured by titration methods. Other experimental parameters were:

Diameter of Reactor Tube	2.8 cm
Sample weight	2.0 g.
Temperature Range	1100-2200 °F
Rate of Heating - rate of equilibration (less than 1 minute)	
Carrier gas - compressed air	
Approximate gas velocity over sample	33.5 cm/min.
Infrared frequency band for SO_2 determinations	1340 cm^{-1}

The resultant ash was also tested to determine what effect heating had upon the "free" lime (CaO) values of the ash, ie, the amount of unreacted calcium oxide present in the ash after gas evolution. For a schematic of the experimental set-up, see Figure 3-0.

Other measurements determined included the temperature of maximum sulfur dioxide evolution, the rate of evolution and the relative concentration of sulfur dioxide evolved.

B. Results

Both wet-collected KPL and dry-collected CM evolve sulfur dioxide when heated in an oxidizing atmosphere. Carbon dioxide and water vapor are also evolved. The rate of evolution of sulfur dioxide is temperature dependent; evolved concentrations, however, are dependent both on temperature and on the flow rate of air which causes dilution effects on the evolved gases.

Sulfur dioxide slowly evolves from CM when the ash is heated to temperatures over 1800°F. The rate of evolution increases with increasing temperatures until approximately 2180° $\pm$ 10°F above which the sample melts. For example, under constant air flow and at 2130 $\pm$ 10°F, 43% of the total sulfur dioxide present in the sample (6.32 wt. %) is evolved within 5 minutes, while at 2180 $\pm$ 10°F, over 90% of the total sulfur dioxide is evolved in the same time period. If the sample is allowed to remain at 2180 $\pm$ 10°F for 10 minutes, 99% of the total sulfur dioxide is evolved. Therefore, this temperature may be considered the lowest temperature of maximum evolution, ie, the maximum

amount of sulfur dioxide is evolved in the shortest time period. Also, at this temperature the physical integrity of the sample is not affected. The relationships between temperature and the amount of sulfur dioxide evolved for sample CM are shown graphically in Figure 3-1. The concentration of the evolved sulfur dioxide gas is dependent upon the air flow sweeping the sample. By adjusting the rate of air flow, concentrations of nine to thirteen percent sulfur dioxide were obtained. These concentrations are within the optimum concentration range of sulfur dioxide for use as a sulfuric acid plant feed stock. Figures 3-4 through 3-8 illustrate the relative concentrations and total amounts of sulfur dioxide evolved at various temperatures. The sulfur dioxide gas evolved upon heating is relatively pure. Only two impurities were noted; they are carbon dioxide (CO_2) and water vapor. Both impurities are completely evolved within the first three minutes of heating and can be removed at much lower temperatures--approximately 1380°F. Also, in sulfuric acid manufacture, carbon dioxide is usually considered an inert gas which does not disturb the process. Therefore, the sulfur dioxide gas released when heating sample CM in an oxidizing atmosphere can be considered to be a pure acid feed stock that is evolved in a short time and in large quantities.

Sulfur dioxide begins to evolve from dried KPL ash at 1700 $\pm$ 10°F. Like CM, the rate of evolution increases with increasing temperatures but for KPL this increase is much less rapid (See Figure 3-2). Although KPL begins to melt at 2150 $\pm$ 10°F, a slightly lower temperature than the initial melting point of CM, longer times were required to evolve the same fraction of the theoretical yield of sulfur dioxide when heating KPL than were observed when heating CM. The theoretical total yield of sulfur dioxide in sample KPL is 10.34% by weight. For example, at 2150 $\pm$ 10°F, 96% of the total yield is given off in 20 minutes, while at 2010 $\pm$ 10°F only 24% is evolved in the same time period. The temperature

FIGURE 3-1

THE AMOUNT OF SULFUR DIOXIDE GENERATED BY HEATING SAMPLE CM*
AT VARIOUS TEMPERATURES

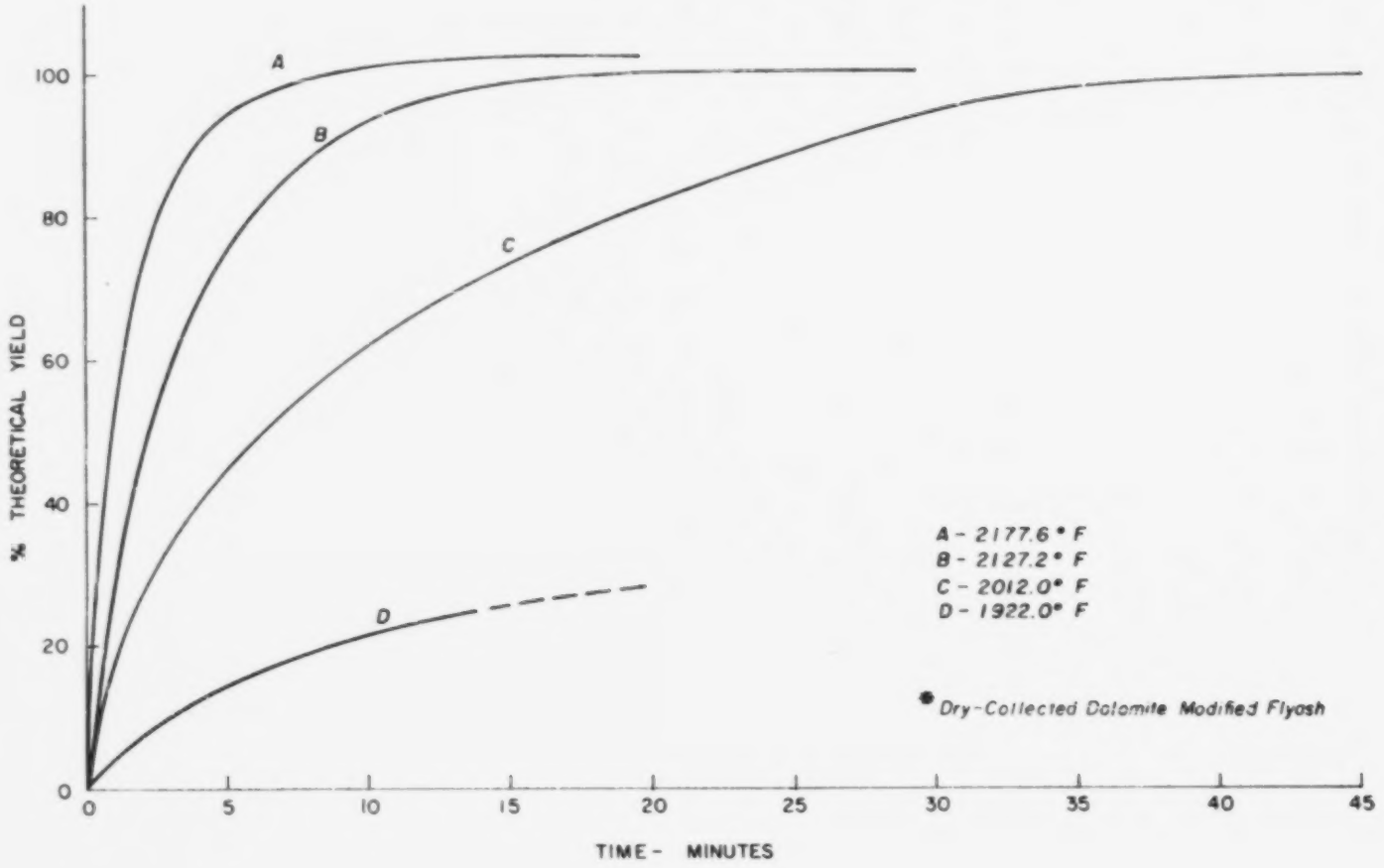
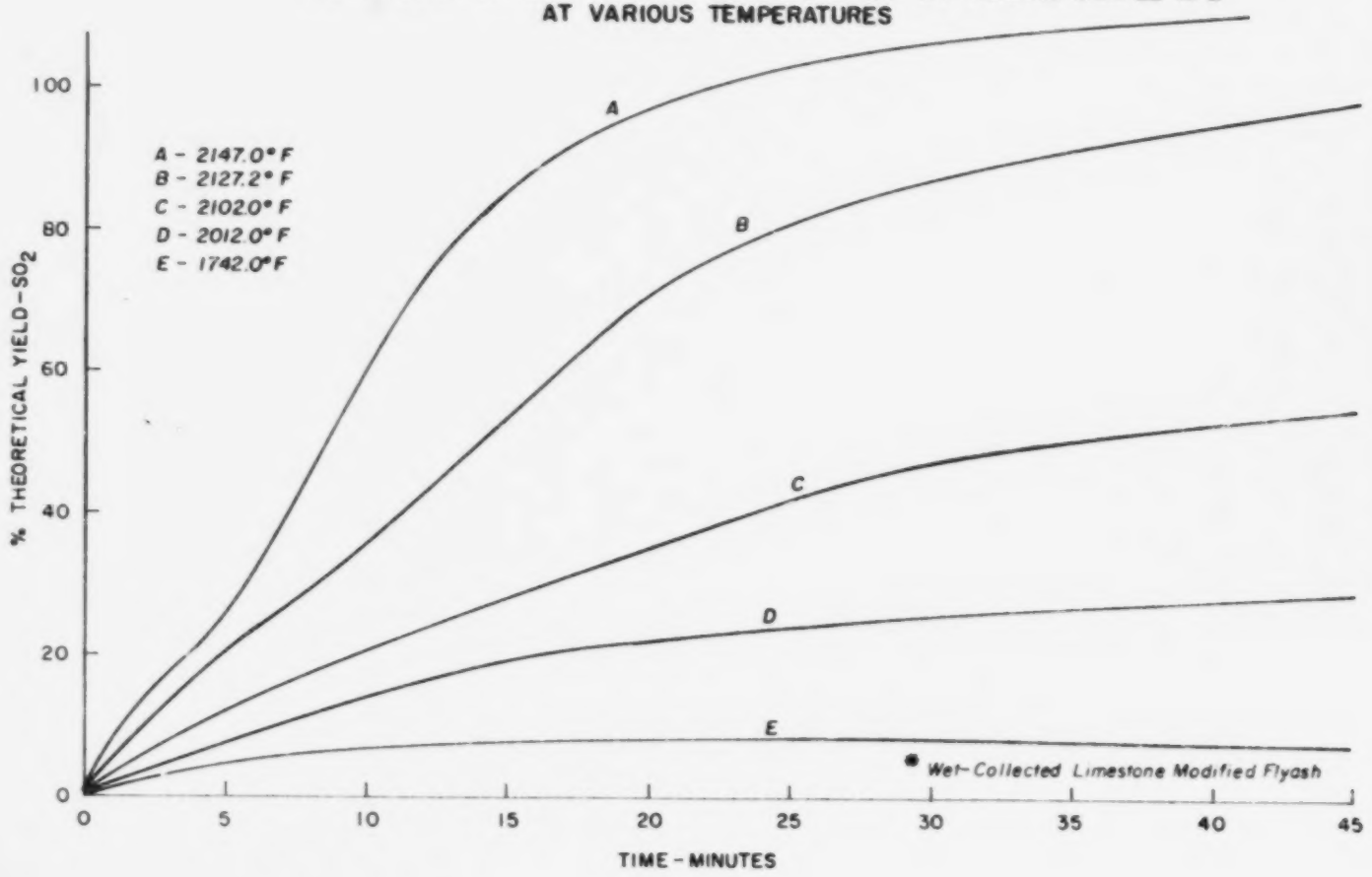


FIGURE 3-2

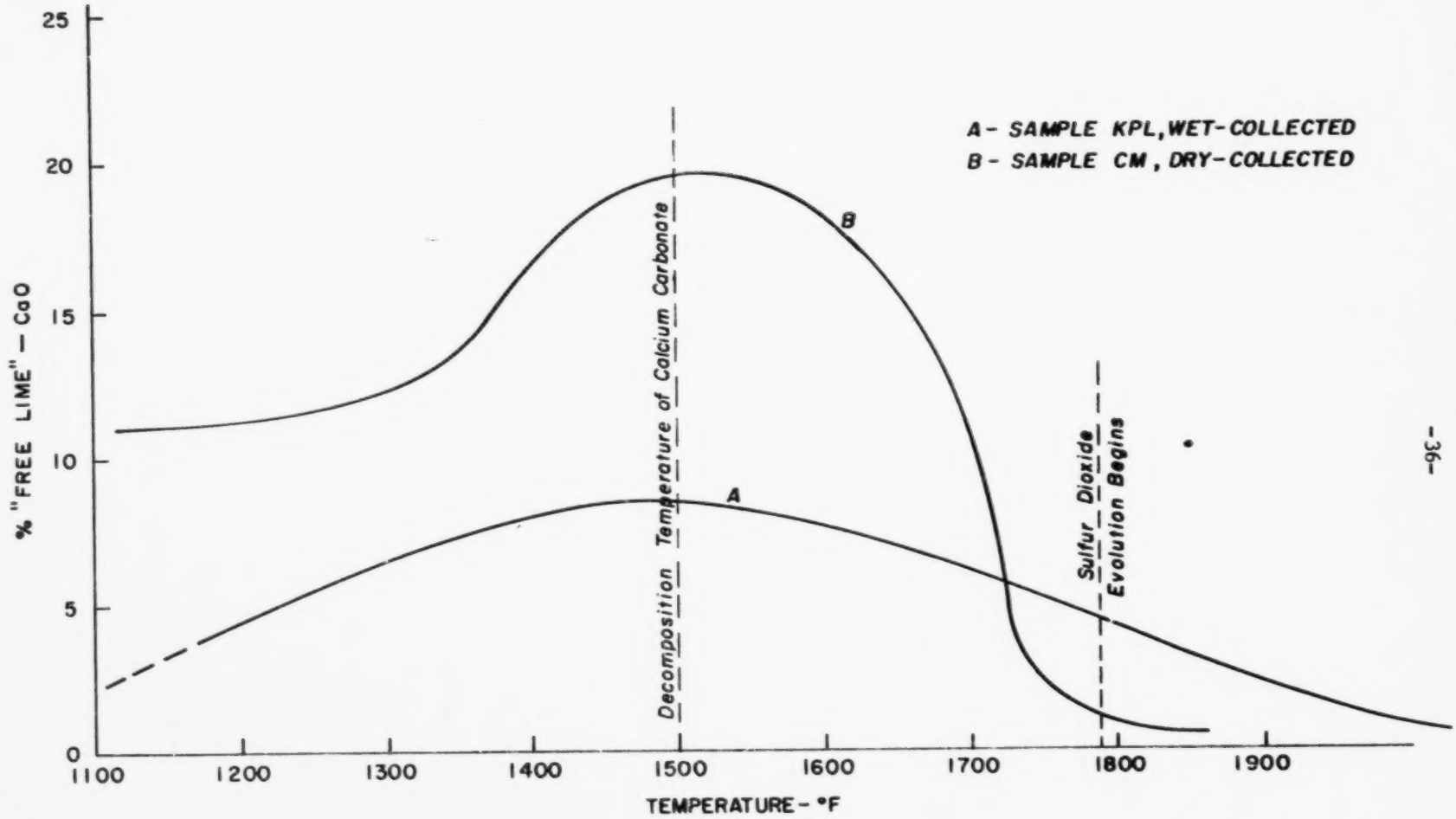
THE AMOUNT OF SULFUR DIOXIDE GENERATED BY HEATING SAMPLE KPL*
AT VARIOUS TEMPERATURES



of maximum evolution of sulfur dioxide is 2150 ± 10°F, 30°F lower than the maximum evolution temperature CM. Figures 3-9 through 3-13 illustrate the relative concentrations and the total amounts of sulfur dioxide evolved from KPL at various temperatures. Particular notice should be given to the late breakdown of one of the sulfurous constituents of KPL which is noted by the infrared spectrometer as the third peak found in Figures 3-9 through 3-13. This late sulfur evolution lengthens the time necessary to drive off the sulfur dioxide from the sample. The origin of this peak of sulfur dioxide evolution cannot be determined under the scope of the present contract and no plausible explanations have been speculated. Even with an extended heating period, however, concentrations of 9 to 13 percent sulfur dioxide have been obtained. Impurities found in the evolved gases are again carbondioixde and water vapor. However, less carbon dioxide is evolved when heating KPL than when heating CM. The average amount of carbon dioxide evolved from KPL is 0.05 grams per gram of sample; when heating CM, 0.135 grams per gram of sample is evolved. Again, both impurities may be fractioned off at temperatures lower than those necessary for sulfur dioxide evolution.

Studies were also performed on both the ashes to determine what effect heating had upon the "free" lime (CaO) content or cementitious capability of each ash. Prior to heating, sample CM contained approximately 9 percent "free" lime--KPL about 2 percent. Measured samples of modified ash were heated under oxidizing conditions and their "free" lime contents were measured at various temperatures (See Figure 3-3). The "free" lime contents of both sample KPL and CM increased in the temperature range of 1290 ± 10°F and 1740 ± 10°F. In this temperature range the "free" lime content of CM doubled, while in the same range, KPL displayed a three-fold increase in CaO. This increase in "free" lime is not a function of sulfur dioxide evolution or the breakdown of calcium sulfates since this increase occurs below the minimum sulfur dioxide evolution temperature. It is the decomposition of uncalcined calcium carbonates ($CaCO_3$) present in

"FREE" LIME CONTENT OF WET AND DRY-COLLECTED MODIFIED FLYASHES



the ash that increases the CaO content of each ash. This increase is compound specific and it is well to note that the maximum increase of "free" lime content for both ashes occurs at the decomposition temperature of calcium carbonate (~1500°F). This "free" lime content decreases at higher temperature due to the dead or hard burning of the lime. Therefore, sulfur dioxide regeneration of modified ash does not beneficiate the cementitious capabilities of the heated ash.

Conclusions

Both dry- and wet-collected modified ash regenerate sulfur dioxide in concentrations favorable to sulfur acid manufacture. To use modified flyash as a sulfuric acid feedstock on an industrial scale, modified flyash may be considered analogous to pyrite. Both raw materials must be roasted or burned in air to produce sulfur dioxide gas; and when the pyrite considered is a by-product from flotation separation, both raw materials are finely sized. Also, the heating temperatures of both materials are somewhat similar (about 1700-2000°F for pyrite and 1900-2200°F for modified ash.) Therefore, under favorable conditions, the gross processing variables of both raw materials are similar and it would initially appear that the cost of producing sulfuric acid from modified flyash is economically similar to the cost of producing sulfuric acid from finely ground pyrite.

From a practical point of view, however, it would take ten times more modified ash to produce the same amount of sulfur dioxide as pyrite. (Pyrite contains 35-52% sulfur; flyash contains about 3.6% sulfur on the average.) Even selling as cheaply as $1 per ton, it would cost $10/amount of SO_2 for a modified ash raw material while the same effective amount of pyrite would cost $7.50. Also, this increase in raw material volume would appreciably increase the production costs, the cost of waste disposal and the initial investment cost. For these reasons the production of sulfuric acid from modified flyash cannot be competitive with existing processes unless a major supplementary use can be made of the non-sulfur bearing portions of the ash.

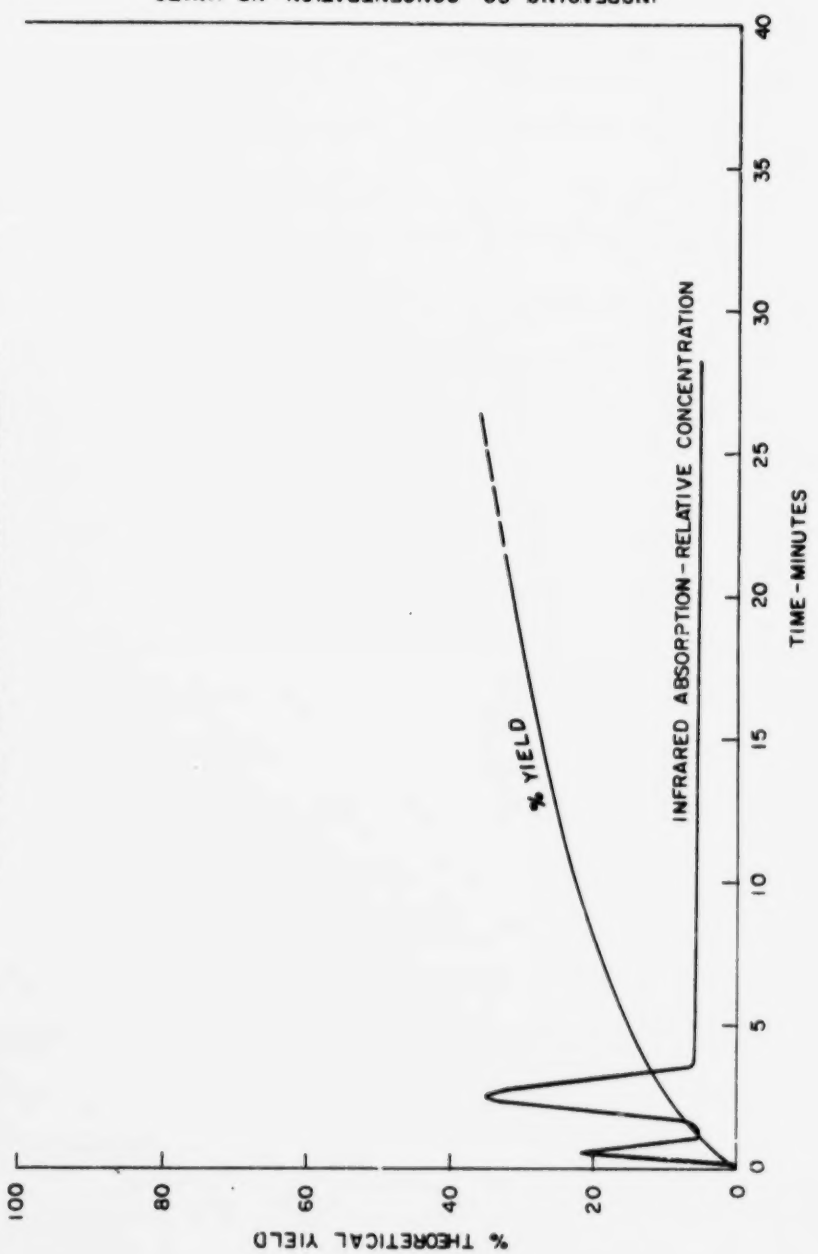


FIGURE 3-4

CM FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 1922.0° F.

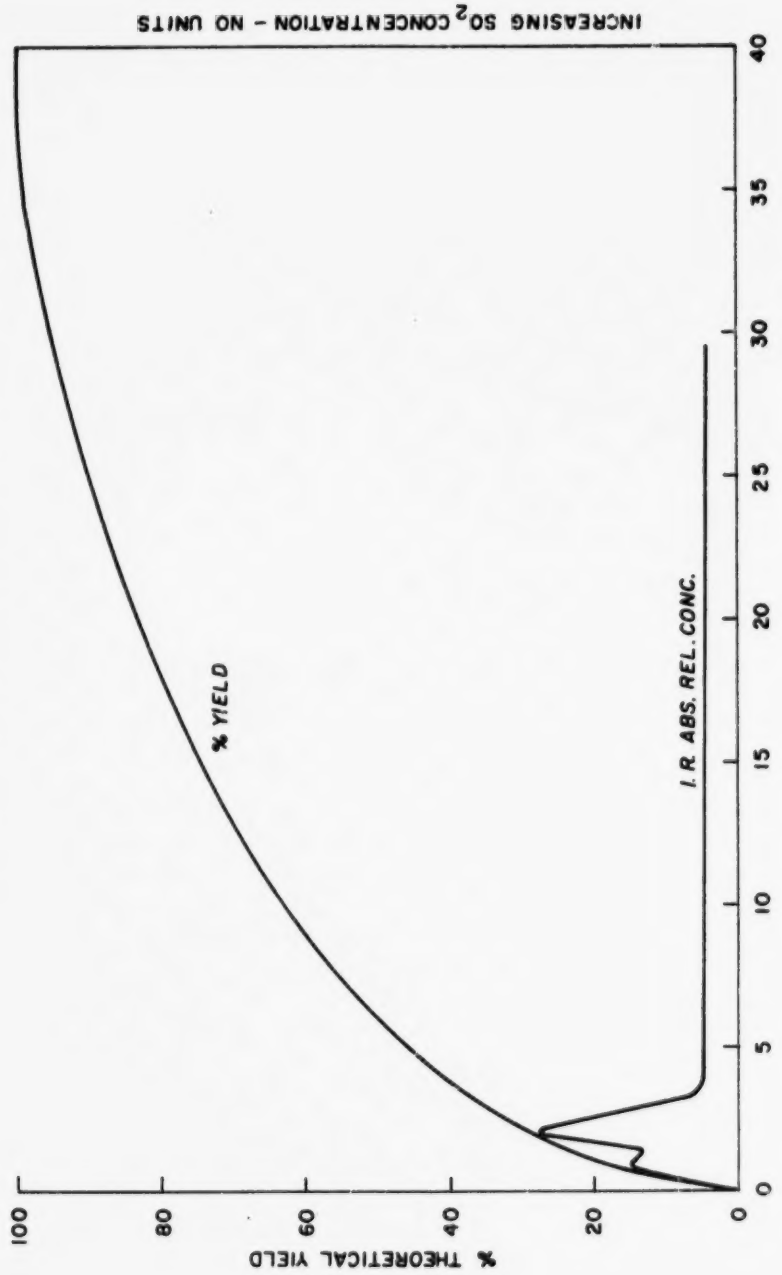


FIGURE 3-5

CM FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2012.0° F.

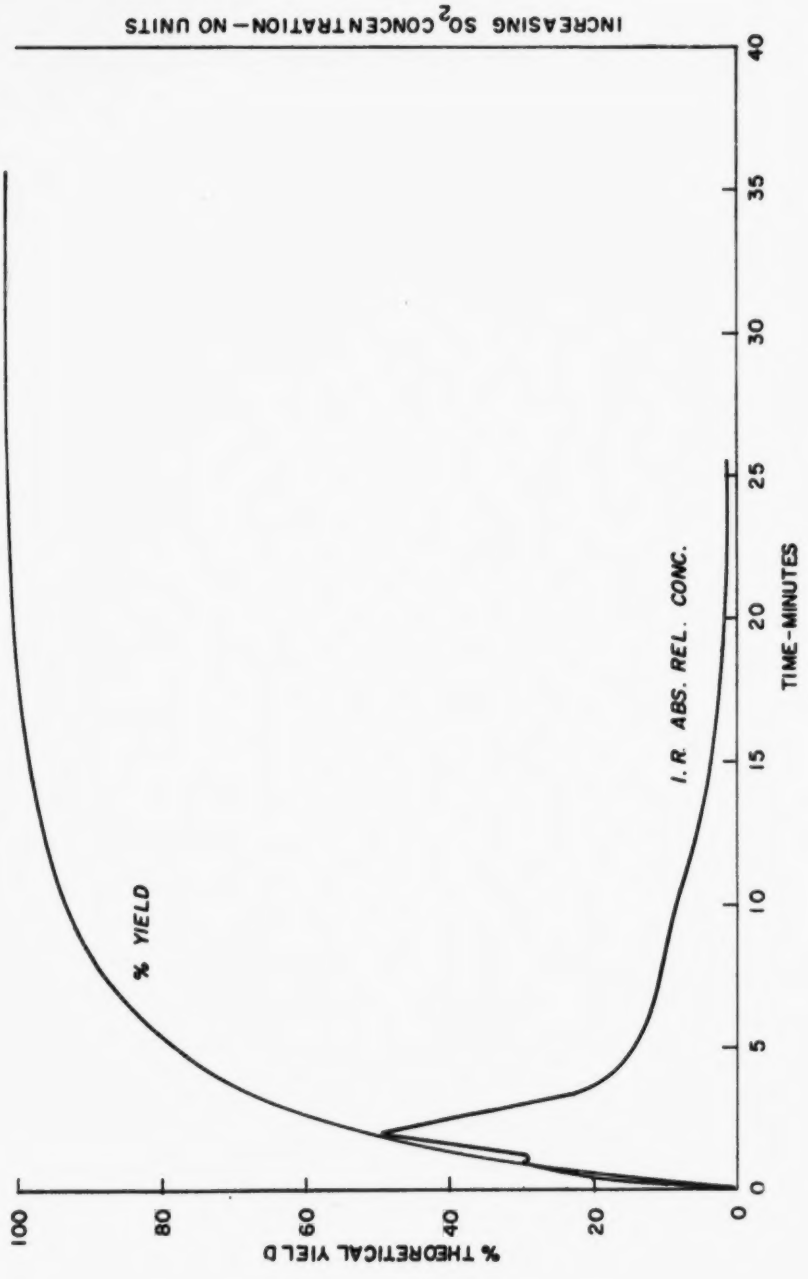


FIGURE 3-6
CM FLYASH
THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2127.2° F.

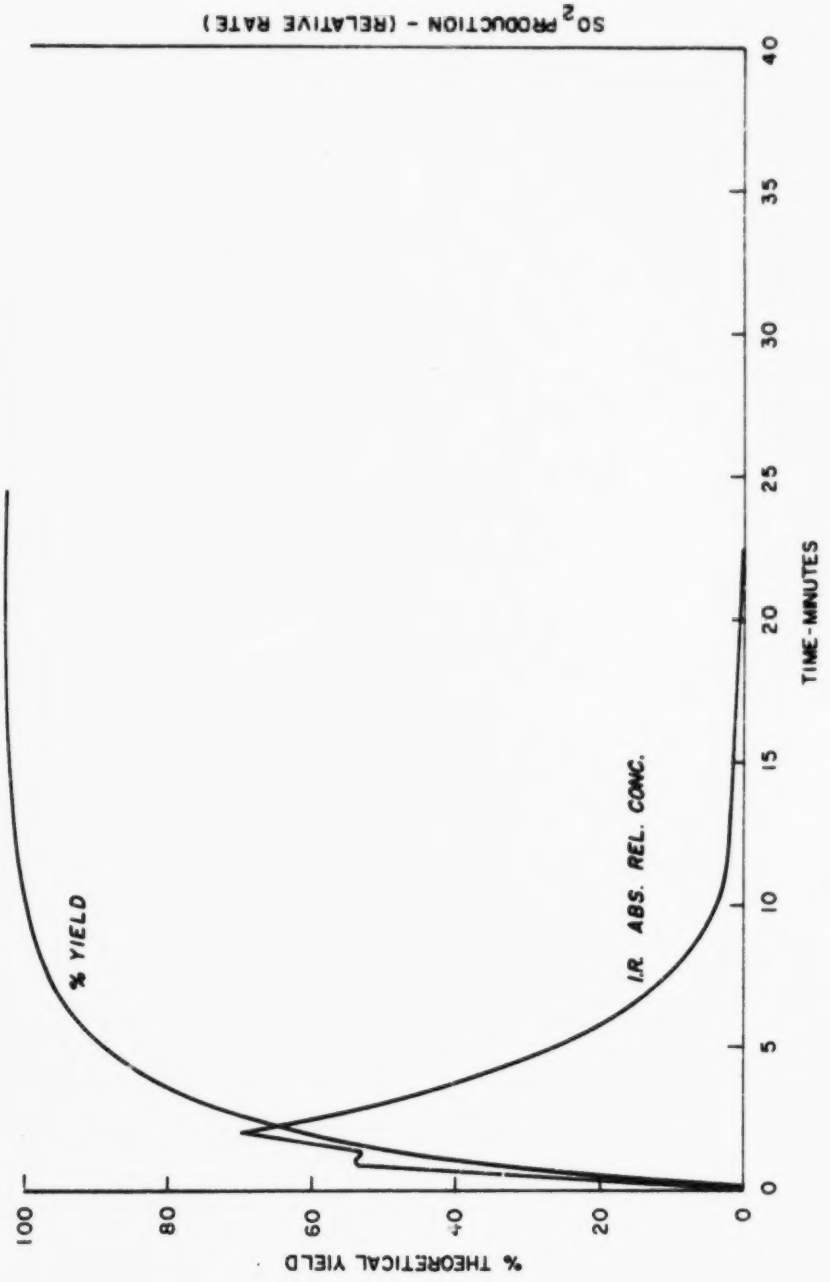


FIGURE 3-7

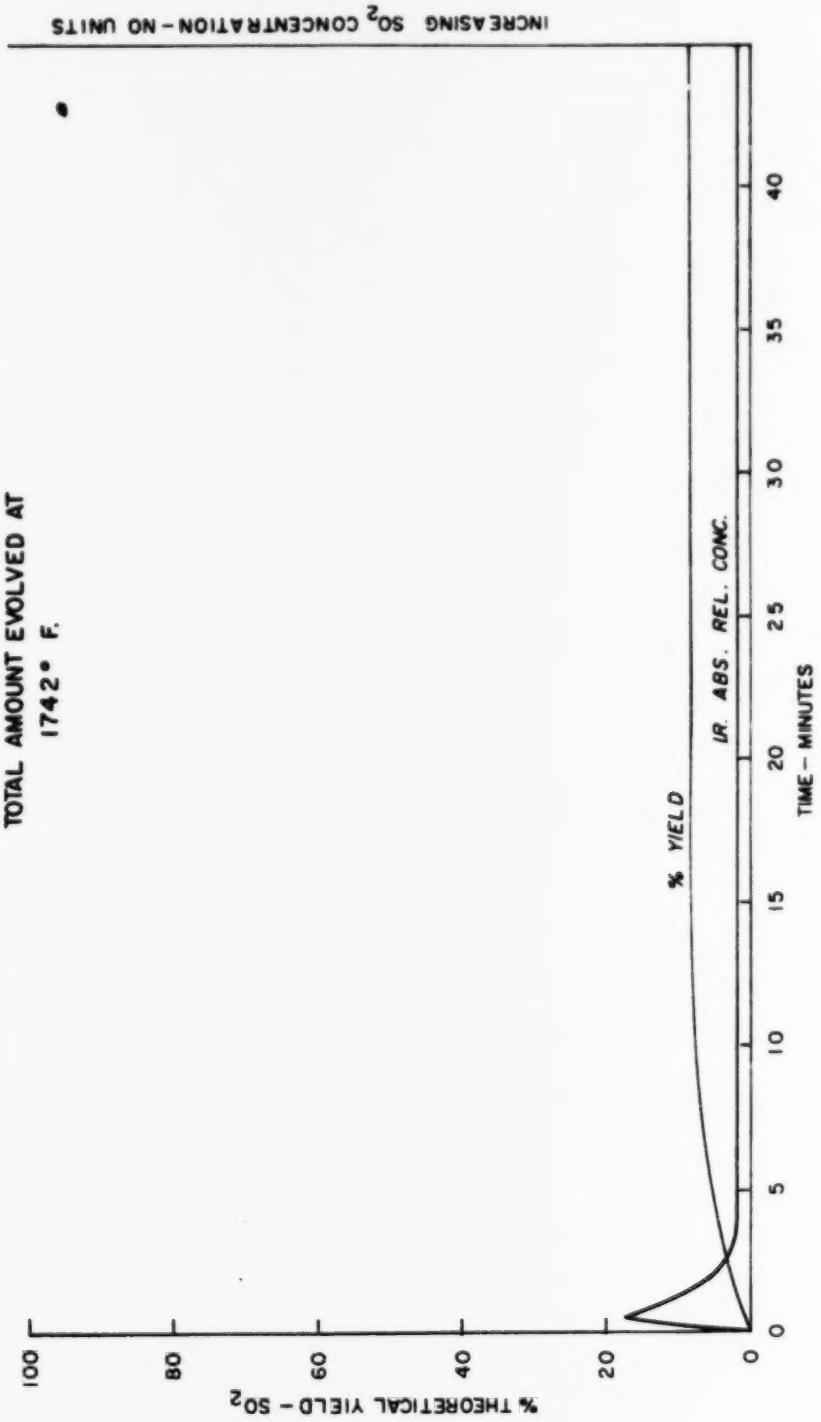
THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2177.6°F.

C-M FLYASH

FIGURE 3-8

KPL FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 1742° F.



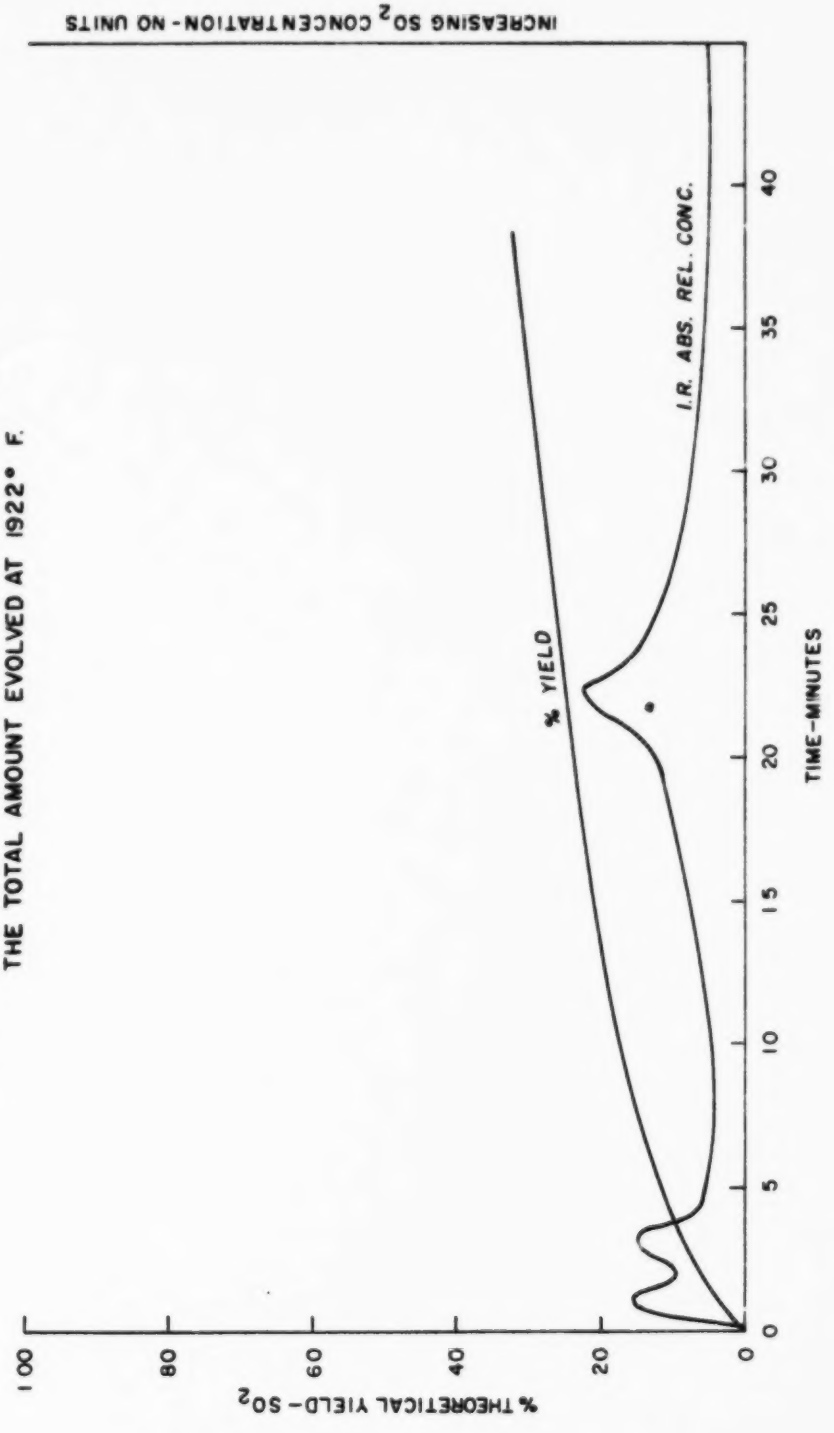


FIGURE 3-9

KPL FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 1922° F.

FIGURE 3-10

KPL FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2012° F.

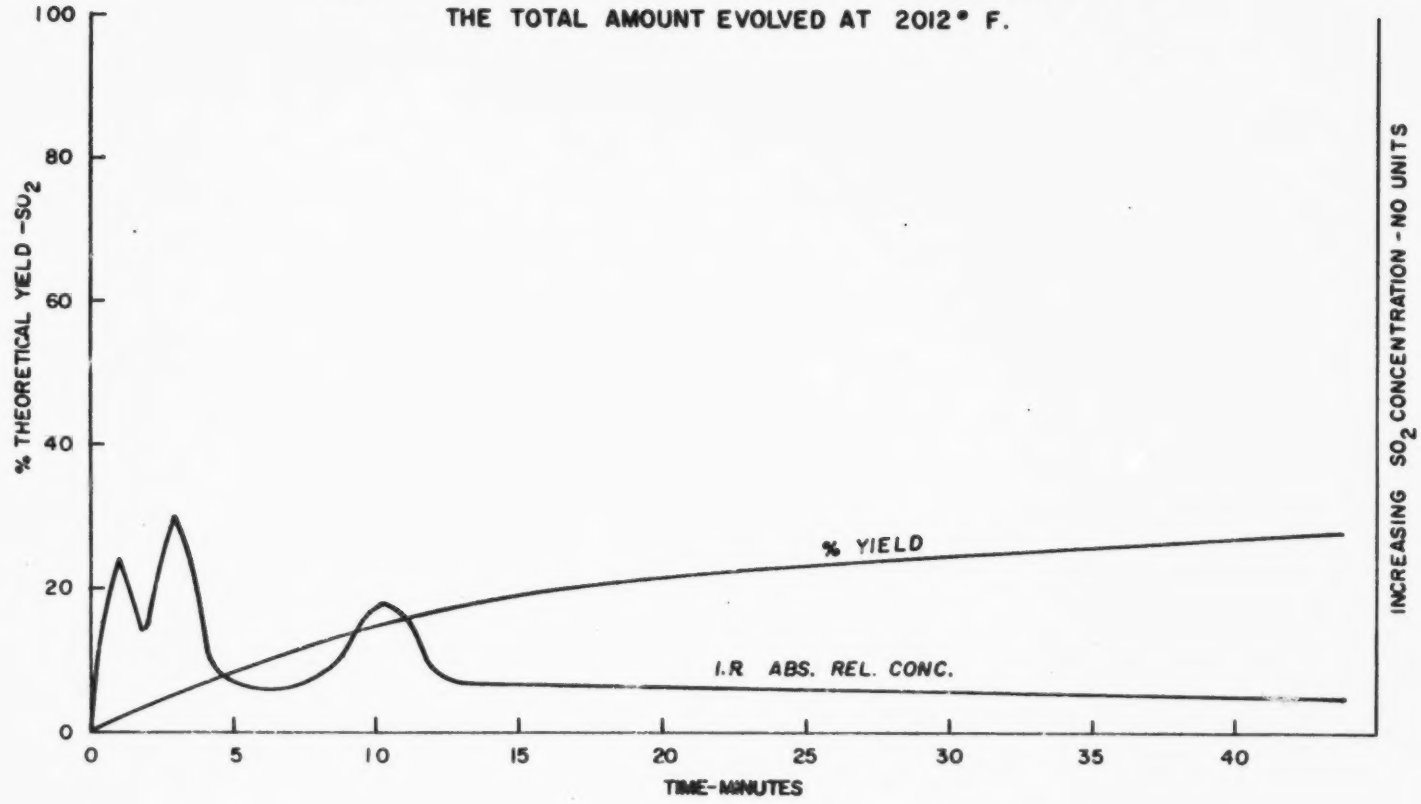
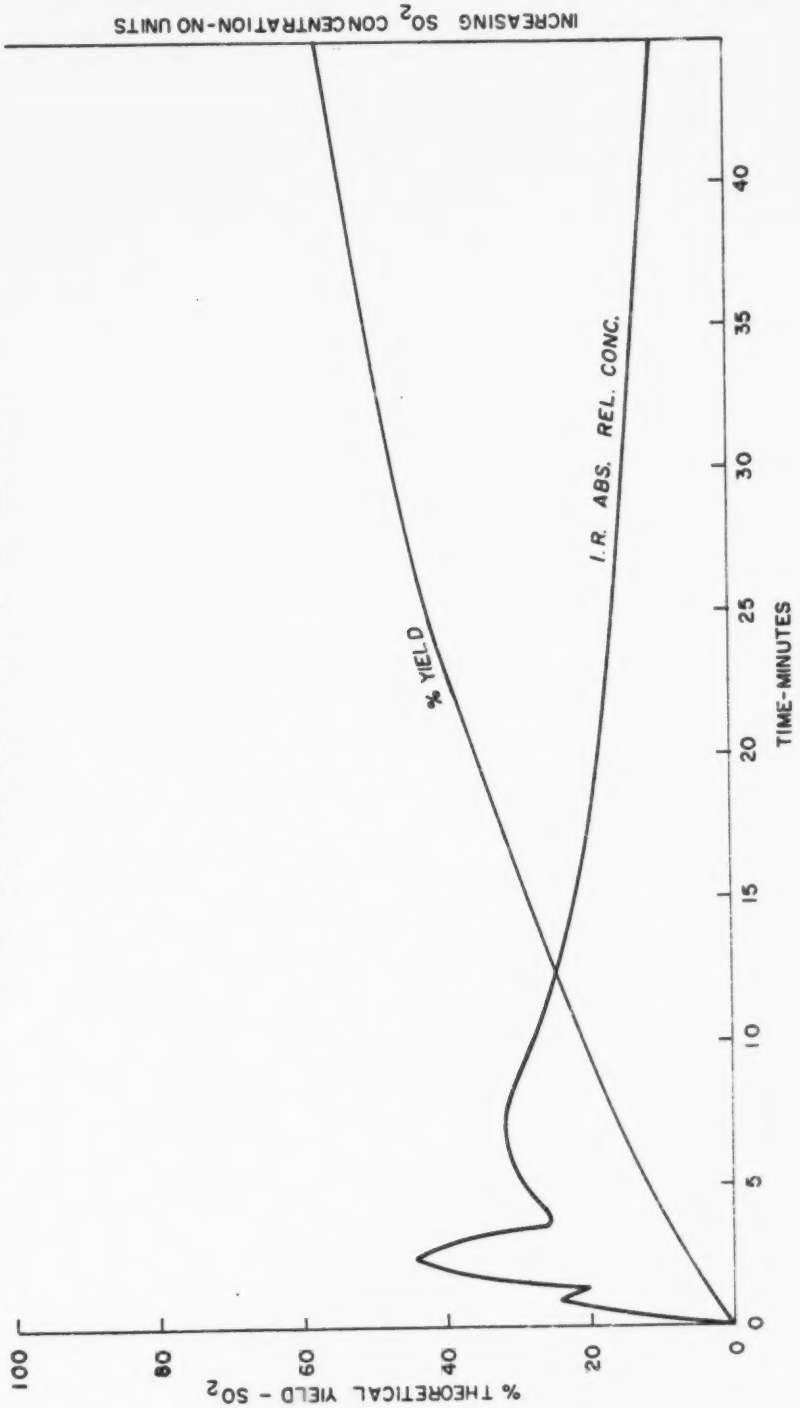


FIGURE 3-11

KPL FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2102.0° F.



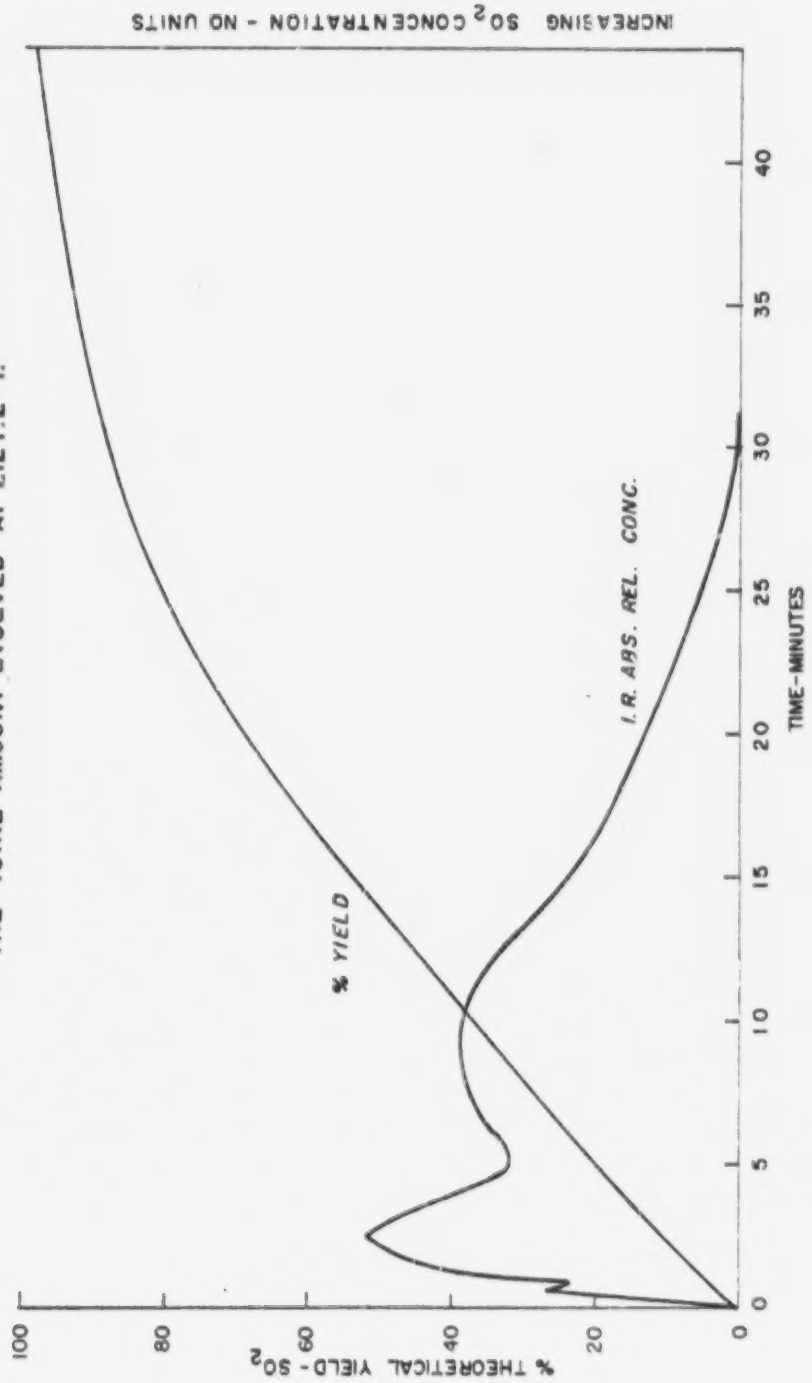


FIGURE 3-12

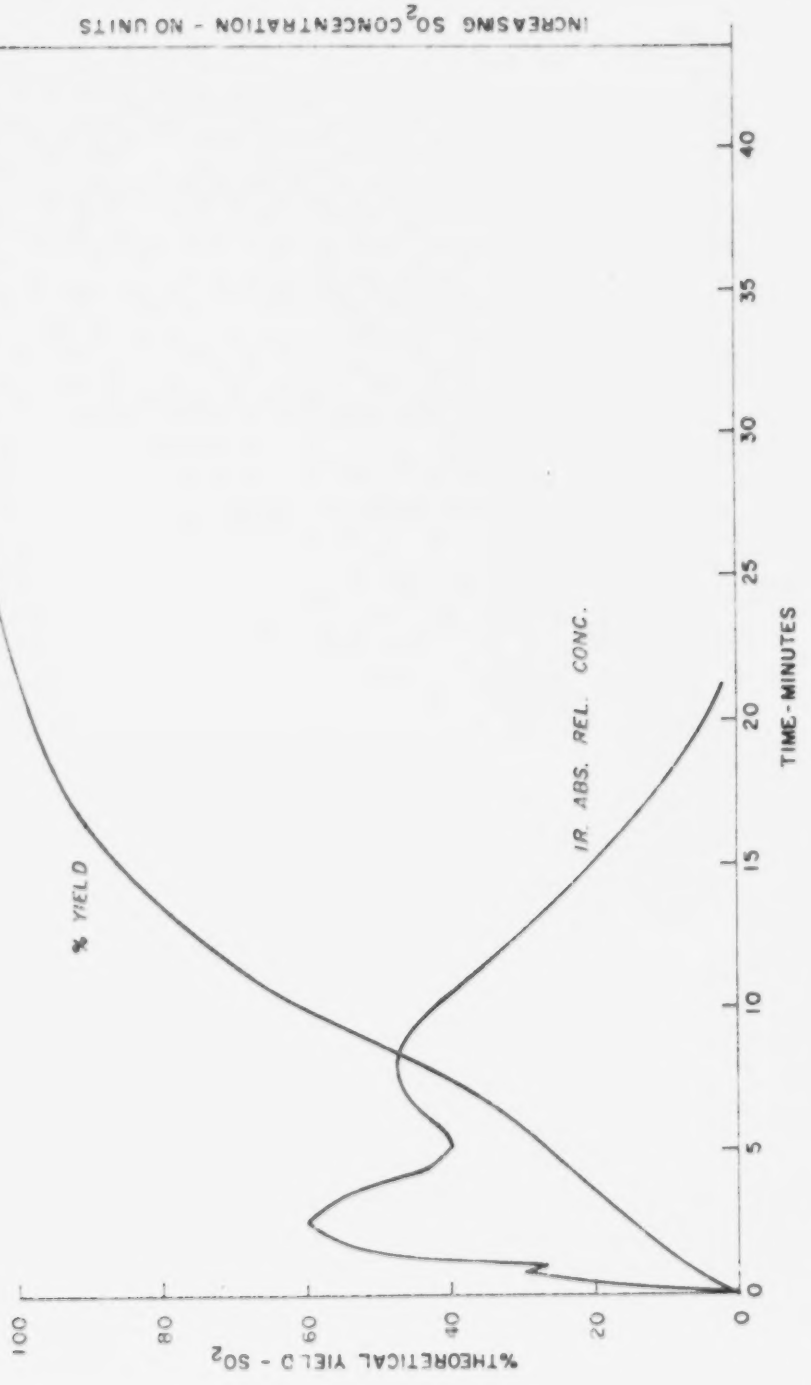
KPL FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2127.2° F.

FIGURE 3-13

KPL FLYASH

THE RELATIVE CONCENTRATION OF SULFUR DIOXIDE EVOLVED AND THE TOTAL AMOUNT EVOLVED AT 2147.0° F.



Sulfur Dioxide Regeneration

3-1 Boynton, Robert S., Chemistry and Technology of Lime and Limestone. Interscience Publishers, Inc., New York, 1967, pp 5-31.

3-2 Karchmer, J. H., "The Analytical Chemistry of Sulfur and Its Compounds," Chemical Analysis. Vol. 29, Interscience Publishers, Inc., New York, 1970.

3-3 Moorehead, D. R. and Taylor, W. H., "Sucrose Extraction Method of Determining Available CaO in Hydrated Lime," ASTM Bulletin. No. 236, 1967, pp 45-47.

3-4 Duecker, Werner W., and West, James R., The Manufacture of Sulfuric Acid. Robert E. Krieger Publishing Co., Inc., Huntington, New York, 1961.

3-5 Connor, J. M., "The Economics of Sulfuric Acid Manufacture," Preprint 6D American Institute of Chemical Engineers, Sixty-First Annual Meeting, Los Angeles, California, December, 1968.

4. MINERAL WOOL

As a result of highly promising data obtained in earlier phases of research, [4-1] mineral wool production was continued under this contract in order to (a) test a wider variety of modified flyashes and (b) produce samples for additional quality testing and comparative economic evaluation. A carbon-arc tilting furnace was used to melt the samples and mineral wool was produced by pouring the molten material from the furnace in a thin stream and into a jet of compressed air. The air imparted a shearing force to the molten mass, breaking the stream into small droplets which were propelled through the air and formed fibrous "tails." Any solid remnants of the original droplets are termed "shot."

A. Modified Flyashes Tested

The modified flyashes tested and their mineral wool production characteristics are given in Table 4-1.

As shown in Table 4-1, the pouring temperature of the modified ashes was approximately 2700°F with the exception of SLD which was poured at 2800°F. All pouring temperatures were below those necessary for wool production from bottom ashes and current commercial raw materials. Blowing pressures ranged between 90 and 95 psig, and were within the range utilized in the previous tests on coal bottom slag and modified flyashes.[4-1]

A significant difference was observed in the production yields from the individual samples. A much higher yield was obtained from sample KPL, the only wet-collected limestone modified flyash available, than from the dolomite flyash. The lowest yield was obtained from sample CM, dry-collected dolomite modified flyash, in which the coal and dolomite were premixed upon entering the combustion area. In comparing the acid/base ratios (percent silica plus percent alumina)/(percent lime plus percent magnesia) sample KPL at 1.30 falls

TABLE 4-1

PRODUCTION CHARACTERISTICS OF MINERAL WOOL

Sample	Type	Acid/Base Ratio	Pouring Temp. °F	Blowing Pressure psig	Yield	Comments
KPL	Wet Collected Limestone Modified	1.30	2700	92	High	Light brown, short fluffy fiber, very little shot
SLD	Wet Collected Dolomite Modified	1.87	2800	90	Moderate	Gray, some brittle fiber, moderate shot
CI	Dry Collected Dolomite, Injected	1.58	2700	93	Moderate	Gray, resilient fiber, moderate shot
CM	Dry Collected Dolomite, Mixed	1.52	2700	95	Low	Gray, fluffy fiber, heavy shot
CU	Unmodified	9.79	3000	95	None	No fiber formed

closest to the generally accepted mineral wool production range of 0.85 to 1.25. SLD and CI (1.87 and 1.58 respectively) had lower yields than KPL.

Although samples CM and CI were produced from the same coal and the same dolomite, a difference in their yields of mineral wool was noted, possibly due to the different methods of introducing the dolomite at the boiler. Sample CM was formed by premixing the dolomite and coal before pulverization and entry into the boiler while sample CI was formed by injection of the dolomite above the flame envelope.

Unmodified ash sample CU was utilized as a control. As shown in Table 4-1, no fiber could be produced even at temperatures as high as 3000°F.

B. Quality Tests

Results of quality tests performed to date are given in Table 4-2. These tests were performed in accordance with the Department of Commerce, Commodity Standards Division: Commercial Standard CS 131-46. All test samples were shaken on a Tyler laboratory screen (6 mesh) prior to quality testing in order to remove any loose shot. A sample of commercial mineral wool was also tested for comparative purposes.

Attached Shot Attached shot is a measure of the shot attached to the fibers or entrapped by them. The shot content of commercial products range from 30 to 40 percent. The dolomite modified flyash samples fall within these limits while mineral wool produced from limestone modified flyash, KPL, has an even lower percentage of attached shot. The attached shot could be removed by regular processing methods used in the mineral wool industry.

Shot formed during the blowing of samples KPL and SLD was collected and reheated to determine if remelting of the shot would be feasible. The mineral wools produced were of the same quality as those obtained from the initial ashes under the same test conditions.

TABLE 4-2

QUALITY TESTS ON MINERAL WOOL

Sample	Average Fiber Diameter	Attached Shot wt. %	Moisture Adsorption wt. %	Odor Emissions	Fire Resistance	Corrosion Retardance
KPL	2.5μ	14.0	0.001	No Apparent Difference	Incombustible	Non-corrosive, no etching
SLD	3.0μ	32.0	0.00	No Apparent Difference	Incombustible	Non-corrosive, no etching
CI	5.6μ	34.0	0.00	No Apparent Difference	Incombustible	Non-corrosive, no etching
CM	5.4μ	36.0	0.00	No Apparent Difference	Incombustible	Non-corrosive, no etching
Commercial	8.4μ	N/A	0.00	No Apparent Difference	Incombustible	Minor Corrosion, no etching

Moisture Adsorption Ten gram samples of each test batch were dried to a constant weight at 120°F in a drying oven and placed in a humidity chamber. The samples were held at 120°F, 95 percent relative humidity for 96 hours and were then immediately reweighed and the percent moisture adsorption by weight determined. As shown in Table 4-2, none of the samples adsorbed a noticeable amount of moisture. These values compared favorably with those found for commercial mineral wool.

Odor Emissions For the odor emissions test, equal volumes of mineral wool samples were separately placed in closed petri dishes beside a 1" x 1" x 1/4" pat of fresh butter. After 24 hours, the pats of butter were smelled and tasted by three laboratory technicians. No apparent difference was found between the test samples and the control.

Flammability Mineral wool test samples were placed on a wire screen and backed with asbestos board. They were then placed above a natural gas-air burner. The hottest point of the flame was adjusted to touch the samples. The temperature was brought to 1600°F and maintained for forty minutes. All of the test samples were rated incombustible.

After the test, it was noted that the wool produced from sample KPL was a lighter color where it had been in contact with the flame. This phenomenon is presumably due to the oxidation of surface of the sample. The commercial wool, however, lightened to a greater degree.

Corrosion Retarding Properties Cold rolled steel strips were covered with mineral wool and placed in a humidity chamber for 96 hours at 120°F and 95 percent relative humidity. All of the modified flyash mineral wools tested proved to retard corrosion of the test strips. No chemical etching of the test occurred although extensive surface rusting and pitting was noticed. The modified flyash mineral wools also showed superior corrosion retarding properties when compared with commercial wool.

Fiber Diameter

Random samples were taken from the modified flyash mineral wools and examined microscopically to determine the fiber diameters and to check for unfavorable crystalline inclusions. Commercial mineral wool was utilized as a control. The most satisfactory mineral wools have average fiber diameters which range from two to ten microns. In this range, they exhibit the softness and resiliency desired. As shown in Table 4-2, all of the modified flyash mineral wools are within this range. It was noted that the commercial wool averaged many more fibers above the range of two to ten microns than did the four modified flyash mineral wools tested. This uniformity of fiber diameter for modified ash base mineral wool is dependent upon a uniform viscosity at pouring temperatures. Although modified ash is composed of distinct particles of lime and flyash, when heated it acts as if it were a homogeneous mixture of silica and lime and, therefore, the melt is more uniform than that obtained from the industrial cupola charge of siliceous and calcareous material.

In addition, microscopic observation indicated that no unfavorable crystalline inclusions existed in any of the modified flyash mineral wool samples.

C. Cost Analysis

The economic feasibility of mineral wool production was estimated based upon information received from Combustion Engineering Company, Inc. Data show that moderate to good profits may be anticipated from modified flyash mineral wool production. A copy of the preliminary production cost estimate can be found in Table 4-3.

For mineral wool selling at $100 per ton and a plant producing six thousand (6,000) tons of mineral wool a year, the cost of production would be about 75% of the final product value. Using these assumptions, the plant payout time is a very attractive 1.5 years. However, because suitable

TABLE 4-3 -55-

WEST VIRGINIA UNIVERSITY
COAL RESEARCH BUREAU
PRELIMINARY PRODUCTION COST ESTIMATE

Date 8-24-71
By K. K. Humphreys

Location N. E. United States
Capital Investment
Total
Less Working Capital N.A.
Less Salvage Value
Depreciable Investment $250,000

Product(s) Granulated Bagged Mineral Wool
Process WVU Coal Research
M B S Index: N.A.
E N R Index: N.A.
Annual Operating Days: 250
Annual Production: 6,000 ton

Raw Materials	Annual Quantity	Unit Cost	$/Year	$/
(1) ash @ 1.5T/T Wool		$1.00/T		$1.53
(2) coke @ 650#/T Wool		$27.00/T		8.78
(3)				
(4)				
(5) Gross Raw Material Cost (Sum of Lines 1 to 4)				10.31
Misc Credits and Debits				
(6) Disposal of reject		$1.00/T		0.53
(7)				
(8)				
(9) Total Debit (Credit)(Sum of Lines 6 to 8):				0.53
(10) Net Raw Material Cost (Line 5 + Line 9)				10.84

Direct Expense	Unit	Quantity	Unit Cost	$/Year	$/
(11) Steam	M lbs	4.2M/T	0.50/M		2.10
(12) Water (recird make-up 10%)	M gal	18M/T	0.10/M		1.80
(13) Air (90 psi @ 102°F)	M gal	9Mcf/T	0.04/Mcf		0.36
(14) Electricity 150 Cfm	KWH	100 KWH/T	0.01/KWH		1.00
(15) Fuel (Coke)	Incurred as raw material				----
(16) Fuel ( )					
(17) Labor	3 men @ $4.00/hr.				12.00
(18) Supervision	@ 15% of labor				1.80
(19) Maintenance	@ 6% of investment/yr			$15,000	2.50
(20) Factory Supplies	@ 1/2% of investment/yr			1,250	0.21
(21) Indirect Overhead	@ 75% labor, supv. main. labor				11.10
(22) Payroll Overhead	@ 30% labor, supv., maint. labor				4.44
(23) Laboratory	@ 5% labor, supv. maint. labor				0.74
(24) Contingencies	@ 2% above costs (2.1-2.23)				1.00
(25) Total Direct Conversion Cost (Sum of Lines 11 to 24)					$40.03
Indirect Expense					
(26) Depreciation	10 yr straight line			$25,000	4.17
(27) Real Estate Taxes & Insurance	@ 2% of investment/yr			$ 5,000	0.83
(28) Depletion Allowances	none				---
(29) Amortization	none				---
(30) Total Indirect Conversion Cost (Sum of Lines 26 to 29):					5.00
(31) Total Conversion Cost (Line 25 + Line 30):					$45.00
(32) Total Operating Cost (Line 31 + Line 10):					55.87
(33) Packing Expense	Bagging - 100# units/$1/100# est.				20.00
(34) TOTAL COST FOB PLANT (Line 32 + Line 33)					75.87 (over)

Estimate does not include buildings and working capital, or shipping costs.

Value of Product - $100/Ton FOB Plant

Plant Payout Time - $\frac{250,000}{169,800}$ = 1.5 yrs.*

*Appears attractive if building costs are not considered.

If buildings are included in the investment figure, payout time will be approximately 3.0 years which is marginal for investment purposes.

Conclusion: Moderate profits can be anticipated from this process. However, the payout time indicates that the investment is not exceptionally attractive in comparison to other investments unless existing buildings can be made available for use.

data was not available, this cost analysis does not include costs of buildings and working capital, shipping cost or pollution control devices. These expenses would increase the plant payout time considerably (eg, considering building costs alone, payout time approximates 3 years). This analysis does not assume recycling of the shot or the practical usage of the sulfur dioxide gas evolved during the heating of modified flyash. If employed, both of these factors could effectively reduce the production costs and payout time. Therefore, if existing buildings can be made available for use and if the resulting sulfur dioxide gas can be marketed, investments in mineral wool production may prove attractivve.

Conclusion

Modified flyash is an excellent raw material for the production of mineral wool. The physical characteristics of wool fibers produced from modified ash equal or excel commercially available mineral wool. They display negligible moisture absorption values and superior corrosion retarding properties and may be rated as incombustible. Also, modified ash based mineral wool is soft, resilient and has uniform fiber diameter. Cost-figures received from a mineral wool manufacturing company show that a modified flyash based mineral wool plant is economically attractive. Also, due to the growing energy crisis, especially with respect to natural gas reserves, more and more construction companies are building electrically heated homes and buildings. Electric heating, however, requires an increased degree of insulation. It is felt that this situation will, in the near future, increase the demand for mineral wool and will make the production of modified ash based mineral wool even more promising.

Mineral Wool

4-1 Lawrence, W. F., et al, "Production of Mineral Wool from Coal Ash Slag," Final Report, Grant No. SWD-9, U. S. Bureau of Mines, Solid Waste Disposal Program, September, 1969.

4-2 Johnson, R. C., "Development of a Process for Making Mineral Wool and Producer Gas from Carbonaceous Shales and Fuel Ashes," Chemical Engineering Thesis, University of Pittsburgh, Pittsburgh, Pennsylvania, 1940.

4-3 Lamar, J. E., Fryling, C. F., Voskuil, W. H., and William, H. B., "Rock Wool from Illinois Mineral Resources," Bulletin 61. Illinois State Geological Survey, Urbana, Illinois, 1934.

4-4 Crawford, T. S., et al, "A Slagging Gas Producer for the Production of Mineral Wool from Rhode Island Meta-Anthracite," Bulletin No. 3, University of Rhode Island Engineering Experimentation Station, 1953.

4-5 Thoenen, J. R., "Mineral Wool," U. S. Bureau of Mines Information Circular 6142. 1929.

4-6 Wood, F. C., "Rock Wool Possibilities in Oklahoma," Bulletin 60. Oklahoma Geological Survey, 1939.

5. SOIL AMENDMENT

The Coal Research Bureau of West Virginia University and the Virginia Polytechnic Institute and State University, Department of Agronomy, entered into a cooperative study to determine the soil amendment and stabilization properties of modified flyash. The scope of this study included the following objectives:

(1) a direct comparison of modified flyash and calcium carbonate ($CaCO_3$) as amendments for increasing soil pH;

(2) a determination of the relationship between the chemical properties of different modified flyashes and increases in soil pH; and

(3) a determination of the effect of modified flyash upon the availability of boron, molybdenum, potassium, phosphorus and zinc in plants which were potted in certain nutrient deficient soils.

The research was divided into two phases--chemical laboratory determinations to study objectives one and two, and greenhouse studies for objective three. Six different flyash samples were studied in phase one for chemical characteristics and neutralizing power. They were:

1. Presque Isle (PID) limestone injected, dry-collected;
2. Drummond Island (DW) dolomite injected, wet-collected;
3. Chevrolet Motor Division Plant (CM) dolomite premixed, dry-collected;
   (CI) dolomite injected, dry-collected;
   (CU) unmodified, dry-collected; and
4. Kansas Power and Light Company (KPL) limestone injected, wet-collected.

The greenhouse experiments (phase two) dealt specifically with sample KPL. This ash was selected because:

1. It was the only ash readily available in sufficiently large quantities;
2. A limestone modified ash would be less susceptible to leaching of potential water pollutants than a dolomitic ash; and

3. This ash was produced in a commercial on-stream process.

From information based on the VPI study, it was concluded that the application of modified ash did increase the pH of acidic soils. However, modified flyash was only half as effective by weight as calcium carbonate in its neutralizing capacity. Also, when added to the soil in proper amounts, modified flyash additions increased the boron supplying power of some boron deficient soils. Further research is being continued to study the causes of neutralization efficiency. A copy of the study report can be found in Appendix I.

Another property of modified flyash is its soil stabilization characteristics. Prior research[5-1, 5-2] has indicated that modified flyash is texturally a silt loam or silt material and that its application would convert both sandy and clay-like soils into loam soils.

Considering the projected availability and low cost of modified ash, its neutralizing powers and soil stabilization properties may find use in the reclamation of strip mines, spoil banks, and other areas which are highly acidic and texturally unable to support plant growth. Its soil amendment characteristics may be utilized agriculturally to regulate soil pH and the boron supplying power of certain soils. In addition, dewatering of the wet-collected modified ash may not be required for direct application of the ash to problem areas. Also, these applications would constitute alarge tonnage utilization of modified flyash.

Soil Amendment

5-1 Wright, James D., Jr., "The Physical Properties of Flyash and Flyash-Soil Mixtures," Preliminary Report, USBM Grant No. G0101677, September, 1971.

5-2 Personal Communication, John Capp, U. S. Bureau of Mines, Morgantown, West Virginia, summer, 1970.

6. NUCLEATED CERAMIC MATERIALS

In conjunction with heating modified ash to evolve sorbed sulfur dioxide, other high-temperature process applications were examined to utilize the remaining "de-sulfurized" ash. The two major areas of investigation were the production of mineral wool (Section 4) and the production of nucleated castable ceramic products. Results have shown that modified flyash can be considered a potential raw material for the production of nucleated or glass-formed ceramics. Ceramic samples produced to date, however, do not display uniform crystal growth and show signs of zoning. These problems could be solved by the addition of specific nucleating agents or by using higher melting temperatures. To produce glass-formed ceramics from modified ash, the raw material was heated until it attained a pouring consistency. The melt was poured into pre-heated graphite molds to prevent thermal shock and subsequent cracking and was then allowed to cool to its temperature of nucleation. This is the temperature at which the nucleating agent (for example, titanium oxide) provides sites or nuclei for crystallization. For modified ash the nucleation temperature is believed to lie in the vicinity of 1500°F. After the desired nucleation period, the temperature of the sample is raised so that crystal growth may occur. When crystallization is completed, the temperature of the sample is reduced slowly to avoid thermal shock until it reaches room temperature.

Since nucleated ceramics can be used in such a wide range of diverse items--from drain pipes to dishes--the production of glass-formed ceramics from modified ash could provide a potential large-scale flyash utilization. However, the large quantity of heat energy required in the production of castable ceramics from modified flyash indicates that the process is economically unfeasible at this time.

Nucleated Ceramic Materials

6-1 Emrich, Barry R., Technology of New Devitrified Ceramics--A Literature Review. Technical Documentary Report No. ML-TDR-64-203, AF Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, September, 1964.

7. FLOTATION

Flotation is a physicochemical technique used to separate physically distinct mineral entities of small particle size. This technique involves the addition of a chemical reagent (collector) to a water and mineral slurry to render a specific mineral surface hydrophobic or water repellent. While the slurry is mechanically agitated, air is induced into the system so that the hydrophobic mineral system collides with and attaches to the air bubbles. This mechanical action, along with the addition of frothing agents, which produce a more stable froth, physically lifts and supports the hydrophobic material which then floats atop the remaining slurry. The concentrate can then be removed by displacement (such as skimming the slurry surface) or mechanical action.

Flotation studies were undertaken as a continuation of the flotation tests performed under Contract PH 22-68-18 to separate either the calcium oxide or sulfur rich portions of flyash from the remaining slurry. As was the case in the previous contract, attempts at froth flotation of specific elements proved relatively unsuccessful. Solutions of soda ash (specifically sodium carbonate (Na_2CO_3)) and soap solutions (eg, sodium oleate) were added to heated and cooled flyash mixtures to no avail. No other sufficiently selective reagent was found. The lack of flotability of lime or sulfur particles may be due to the physical character of modified flyash. According to a report by Battelle Memorial Institute for the Environmental Health Service, it is believed that the lime binds with the ash by forming a calcareous shell around it.[7-1] The sulfur dioxide is then sorbed on and into this shell in such a manner that the three basic constituents are bound together to form discrete particles. The flyash, sulfur and lime constituents, therefore, are not physically distinct (a fact which was also determined by microscopic analysis). For these reasons the separation of limestone modified flyash

into its components by flotation as a means of achieving improved or partial utilization does not appear feasible.

Flotation

7-1 Coutant, R. W., Barrett, R. E., Simon, R., and Lougher, E. H., "Investigation of the Kinetics of Reaction of a Limestone with SO_2 in Flue Gas," Battelle Memorial Institute--Columbus Laboratories. Paper presented at the Dry Limestone Injection Process Symposium. Gilbertsville, Kentucky, June, 1970.

7-2 Aplan, F. F., and Fuerstenau, D. W., "Principles of Non-Metallic Mineral Flotation," Froth Flotation. D. W. Fuerstenau (ed.), AIME, New York, 1960, p 211.

7-3 Glembotskii, V. A., Klassen, V. I., and Plaksin, I. N., Flotation. Primary Sources, New York, 1963.

7-4 Plaksin, I. N., Flotation Properties of Rare Metal Minerals. Primary Sources, New York, 1967.

SUMMARY

Several promising areas for whole utilization of limestone/dolomite modified flyash have been examined. These areas include:

1. Production of autoclaved structural products;

   a) calcium silicate brick - Brick made using mix proportions of 50% modified flyash, 39% silica sand and 11% lime displayed compressive breaking strengths in excess of 7000 psi and exceed ASTM standards for grade SW (severe weathering) brick;

   b) aerated concrete - Lightweight material having the workability of wood and the thermal properties of concrete were produced from mixtures of 90% modified flyash, 10% portland cement and 0.15% aluminum powder; and

   c) poured concrete - Autoclaved concrete material having the same compressive strength but only sixty percent of the bulk density of conventional concrete was produced from mixes of 50% modified flyash, 39% silica sand and 11% lime.

2. Controlled production of sulfur dioxide;

   When heated in an oxidizing atmosphere, relatively large amounts of sulfur dioxide evolve from modified ash. Potential uses are feed stock for the production of sulfuric acid or for the bottling of pure sulfur dioxide.

3. Production of mineral wool insulation;

   Mineral wool fibers produced from modified flyash displayed excellent resiliency, fire resistant and rust retarding properties, and

4. Use of modified ash as a soil amendment;

   Application of modified flyash has neutralized acidic soils and has increased the boron supplying power of some boron deficient soils.

APPENDIX I

1971

ANNUAL REPORT

ON

MODIFIED FLY ASH INVESTIGATIONS

CONDUCTED BY

THE AGRONOMY DEPARTMENT

RESEARCH DIVISION

VIRGINIA POLYTECHNIC INSTITUTE

AND STATE UNIVERSITY

IN COOPERATION WITH THE

UNITED STATES DEPARTMENT OF INTERIOR

BUREAU OF MINES

PREPARED BY

DAVID C. MARTENS

ASSOCIATE PROFESSOR OF AGRONOMY

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AVAILABILITY OF SELECTED NUTRIENTS IN MODIFIED FLY ASH AND NEUTRALIZING POWER OF THE BY-PRODUCT

INTRODUCTION

Attempts to control SO_2 in flue gases have resulted in large-scale testing of the limestone injection process. The availability of high lime fly ash from these sources and the probability that the amount of this material will increase make its use in agriculture attractive. Therefore, research was undertaken to evaluate agronomic properties of fly ash. The objectives of the research were:

1) To compare modified fly ash with calcium carbonate ($CaCO_3$) as amendments for increasing soil pH.

2) To relate chemical properties of modified fly ash to increases in soil pH due to application of the by-product.

3) To determine the plant availability of boron (B), potassium (K), molybdenum (Mo), phosphorous (P), and zinc (Zn) in modified fly ash.

THE NEUTRALIZING POWER OF MODIFIED FLY ASH

Research has shown that acidic soils must be neutralized in order to attain high yields of certain crops. Calcitic and dolomitic limestones have been applied most frequently to increase the pH of acidic soils. Industrial by-products, such as paper mill sludge, have been used as liming materials in localized areas. The research reported herein was initiated to obtain a preliminary evaluation of the suitability of modified fly ash as a liming material.

Methods and Materials

Three acidic soils varying widely in buffer capacity were selected for a laboratory equilibration study. The soils selected for the study were Davidson clay loam, Marlboro fine sandy loam, and Tatum silt loam. The soils were passed through a 10 mesh screen in preparation for the equilibration study.

Equilibration study. Increments of calcium carbonate ($CaCO_3$) ranging from 0 to 210 milligrams (mg) and two levels of six modified fly ash samples (Table 1) were mixed in duplicate with 30 gram (g) portions of the sieved soils. The mixtures were placed in plastic bags and were watered to approximately field moisture capacity. The bags then were partially sealed with a rubber band to avoid excessive water loss. The watering procedure was repeated 28 and 60 days after the initial wetting of the mixtures. The mixtures were dried in preparation for pH determinations after an equilibration period of 85 days.

Laboratory determinations. The pH of soil: fly ash mixtures was determined with a Beckman Zeromatic pH meter using a 1:2 soil-to-0.01 molar (M) calcium chloride ($CaCl_2$) ratio and a 1 hour equilibration period. The procedure is described in detail by Peech[1]. For determination of neutralizing capacity, 2 gram subsamples of modified fly ash were equilibrated with 50 milliliters (ml) of distilled water for 11 hours, heated for one hour on a steam plate, and titrated to pH 6.5 with 0.01 normal (N) hydrochloric acid (HCl). The titration and heating procedures were repeated four times. The neutralizing capacity is reported as the total amount of hydronium ions (H_3O^+) consumed during the four titrations.

The modified fly ash samples were prepared for aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg) determinations by a sodium carbonate (Na_2CO_3) fusion procedure[2]. One gram samples were fused in platinum crucibles

with 6 grams sodium carbonate. The fusion product was taken up in 35 ml of 6 N HCl and dried. The acidifying and drying steps were repeated to assure dehydration of silica. The dried sample was transferred to polyethylene tubes with 0.5 N HCl and the mixture was centrifuged. The acidification with 0.5 N HCl and centrifugation were repeated. The concentrations of Ca, Fe, and Mg in 100 ml of the supernatant were determined by atomic absorption spectrophotometry.

The total amount of aluminum and iron in 5 ml of the supernatant was determined as outlined in an unpublished procedure by Rich and Singh[3]. A 5 ml aliquot of the sample in 0.5 N HCl was transferred to a 125 ml Erlenmeyer flask. Five milliliters of 0.5 N NaOH, 10 ml of 0.05 M sodium EDTA, 25 ml of an ammonium acetate-acetic acid buffer solution (pH 4.8), and 25 ml of deionized water were added to the flask. The flask was shaken, was heated to a boil, and was cooled to room temperature. Ten drops of a sulphosalicylic solution were added to the mixture and the sample was titrated to a light brown endpoint with 0.025 M ferric chloride ($FeCl_3$) to determine the excess EDTA. The aluminum content of the sample was obtained by subtraction of the iron content, determined by atomic absorption spectrophotometry from the total aluminum and iron content determined as described above.

Results and Discussion

Application of calcium carbonate ($CaCO_3$) increased the pH of the three acidic soils as expected (Table 2). Generally, the pH of the soils varied proportionally to the level of $CaCO_3$ application. The pH of the soils was also increased by application of modified fly ash (Table 3). In all cases, the 1800 mg level of modified fly ash caused a higher soil pH than the 300 mg level.

A soil pH of 6.8 was obtained in the Davidson clay loam by application of 150 mg of $CaCO_3$ (Table 2) or by application of 300 mg of modified fly ash

samples PID and CM (Table 3). These data show that the two modified fly ash samples were approximately one-half as efficient as $CaCO_3$ in increasing the pH of the Davidson soil. The other samples of modified fly ash were less effective in increasing the pH of the soil. The neutralizing power of the modified fly ash samples was higher than that reported for unmodified fly ash[4] or than that obtained for the unmodified fly ash sample CU used in this study (Table 3).

The results of the equilibration study show that samples PID, CI, and CM have a higher neutralizing power than samples DW, CU, and KPL (Table 3). A similar trend was shown by neutralizing powers determined by the titration procedure (Table 4). It can be concluded from these results that the titration procedure could be used to depict modified fly ash samples which differ widely in neutralizing power. The overall lack of agreement between the two procedures shows that the titration procedure would be unsuitable for estimating the neutralizing power of samples where high accuracy is required.

Modified samples containing the highest amounts of total calcium (Ca) and magnesium (Mg) have the highest neutralizing power (Tables 3 and 5). This relationship implies that samples containing the highest amount of free calcite or dolomite have the highest neutralizing power. Verification of this implication requires further knowledge regarding the mineralogical composition of the modified fly ash samples.

It was reasoned that the variables, neutralizing power determined by the titration procedure and the contents of aluminum , calcium, iron, and magnesium might give a good predicition of the neutralizing power of modified fly ash. The results of the elemental composition analyses indicate that the samples are very high in total calcium and magnesium compared to aluminum and iron (Table 5). It seems likely that the neutralizing power of the calcium and magnesium compounds will mask the neutralizing power of the aluminum

and iron. The relationship will be subjected to multiple correlation and regression analyses for more detailed study.

THE AVAILABILITY OF BORON, POTASSIUM, MOLYBDENUM, PHOSPHORUS, AND ZINC IN MODIFIED FLY ASH

Research has shown that application of selected samples of fly ash to soil has beneficial effects on plant growth. Certain samples of fly ash have been shown to correct boron and zinc deficiencies and to partially correct potassium (K), molybdenum (Mo), and phosphorus (P) deficiencies [5,6,7]. The research reported below was designed to determine the effect of modified fly ash application to soil on the plant availability of these elements.

Methods and Materials

Five soils were obtained for these experiments from locations near Blacksburg, Charlotte Courthouse, Orange, and Tazewell, Virginia. In preparation for the greenhouse research, the soils were passed through a stainless steel screen with one centimeter openings, mixed, and stored in plastic bags. Use of this procedure avoided excessive drying of the soils, which may affect nutrient availability.

Boron greenhouse experiment. Five treatments applied to a Tatum silt loam were a check and two levels of boron as $Na_2B_4O_7 \cdot 10H_2O$ and as modified flyash. The amendments for the treatments and reagent grade compounds containing 52.5 mg N, 231 mg P, 210 mg K, 105 mg Mg, 138 mg S, 0.42 mg Mo, 18.9 mg Zn, 15.8 mg Mn, and 4.2 mg Cu were mixed with portions of the moist Tatum soil equivalent to 2100 grams of dry soil. The amended soils were placed in plastic lined pots and the pots were arranged in a completely random design with three replications.

Thirty 'Williamsburg' alfalfa seeds were planted in each pot and when seedlings were approximately three centimeters tall; they were thinned to 15 plants per pot. The pots were watered daily to approximately field moisture capacity throughout the experiment. Supplemental potassium, magnesium,

and sulfur were added to the pots at levels of 105, 52.5, and 69 milligrams, respectively, during the growth period. The top growth of alfalfa was harvested after an overall growth period of 74 days.

Potassium greenhouse experiment. Six treatments applied in triplicate to a Groseclose silt loam were a check, one level of potassium chloride (KCl), one level of $CaCO_3$, one level of both potassium chloride and $CaCO_3$, and two levels of modified fly ash. The amendments for the treatments and reagent grade compounds containing 52.5 mg N, 231 mg P, 105 mg Mg, 138 mg S, 0.42 mg Mo, 18.9 mg Zn, 15.8 mg Mn, 3.2 mg B and 4.2 mg Cu were mixed with portions of the moist Groseclose silt loam equivalent to 2100 grams of dry soil. The amended soils were placed in plastic lined pots and the pots were arranged in a completely random design.

Thirty 'Williamsburg' alfalfa seeds were planted in each pot and when seedlings were approximately three centimeters tall, they were thinned to 15 plants per pot. The pots were watered daily to approximately field moisture capacity throughout the experiment. Supplemental magnesium and sulfur were added to each pot at levels of 52.5 and 69 mg during the growth period. Alfalfa top growth was harvested after an overall growth period of 74 days.

Molybdenum greenhouse experiment. Six treatments applied in triplicate to a Cecil fine sandy loam were a check, two levels of $Na_2MoO_4 \cdot 2H_2O$, one level of $CaCO_3$, one level of both $Na_2MoO_4 \cdot 2H_2O$ and $CaCO_3$, and one level of modified flyash. The amendments for the treatments and reagent grade compounds containing 52.5 mg N, 231 mg P, 210 mg K, 105 mg Mg, 138 mg S, 18.9 mg Zn, 15.8 mg Mn, 3.2 mg B, and 4.2 mg Cu were mixed with portions of the moist Cecil soil equivalent to 2100 grams of dry soils. The amended soils were placed in plastic lined pots and the pots were arranged in a random design.

Eight soybean seeds, variety V66-318, were planted in each pot and,

when seedlings were approximately 5 centimeters tall, they were thinned to five plants per pot. The pots were watered daily to approximately field moisture capacity throughout the experiment. Supplemental potassium, magnesium, and sulfur were added to all pots at levels of 105, 52.5, and 69 mg, respectively, during the growth period. The top growth of soybeans was harvested after an overall growth period of 45 days.

Phosphorus greenhouse experiment. Six treatments applied in triplicate to a Groseclose silt loam were a check, one level of $Ca(H_2PO_4)_2 \cdot H_2O$, one level of $CaCO_3$, one level of both $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaCO_3$, and two levels of modified fly ash. The amendments for the treatments and reagent grade chemicals containing 105 mg N, 105 mg K, 105 mg Mg, 138 mg S, 3.2 mg B, 18.9 mg Zn, 15.8 mg Mn, and 4.2 mg Cu were mixed with portions of the moist Groseclose soil equivalent to 2100 grams of dry soil. The amended soils were placed in plastic lined pots and the pots were arranged in a completely random design.

Eight 'Pioneer 3369A' corn seeds were planted in each pot and when seedlings were approximately 4 centimeters tall, they were thinned to 4 plants per pot. Supplemental nitrogen, potassium, magnesium, and sulfur were applied to all pots at rates of 315, 105, 105, and 138 mg, respectively, during the growth period. The top growth of corn was harvested after an overall growth period of 43 days. Each pot was watered daily throughout the growth period.

Zinc greenhouse study. Six treatments applied in triplicate to a Westmoreland silty clay loam were a check, one level of $ZnSO_4 \cdot 7H_2O$, one level of elemental sulfur, one level of $CaCO_3$, one level of modified fly ash, and one level of both $ZnSO_4 \cdot 7H_2O$ and $CaCO_3$. Amendments for the treatments and reagent grade compounds containing 105 mg N, 105 mg K, 116 mg P, 105 mg Mg, 138 mg S, 3.2 mg B, 15.8 mg Mn, and 4.2 mg Cu were

mixed with portions of the Westmoreland soil equivalent to 2100 grams dry soil. The amended soils were placed in plastic lined pots and the pots were arranged in a completely random design.

Eight 'Pioneer 3369A' corn seeds were planted in each pot and when seedlings were approximately 4 centimeters tall, they were thinned to 4 plants per pot. Supplemental nitrogen, potassium, magnesium, and sulfur were applied to all pots at rates of 315, 105, 105, and 138 mg, respectively, during the growth period. The top growth of corn was harvested after an overall growth period of 43 days. Each pot was watered daily throughout the growth period.

Laboratory analyses. Plant tissue from the various greenhouse experiments was dried at 70°C for 48 hours and ground to pass a 20 mesh screen. Boron in the dried sample was determined by a modification of the curcumin procedure [8]. A one gram subsample of the ground tissue was ashed at 450°C for 2.5 hours and the ash was dissolved in 100 ml of 0.3 N nitric acid (HNO_3). Potassium in the acidic sample was determined by atomic absorption spectrophotometry and phosphorus by a molybdivanadophosphoric acid procedure[9]. Zinc in the ground sample was determined by the procedure outlined by Schnappinger et al.[10].

The modified fly ash samples were prepared for boron, potassium, phosphorous and zinc analyses by a modification of the Kanehiro and Sherman procedure[2] as outlined in a previous section of this report. The boron in the 0.5 N hydrochloric acid leachate of the fusion mass was determined by a carmine procedure[11]. Potassium and zinc in the acidic solution were determined by atomic absorption spectrophotometry and by a molybdenum blue colorimetric method[12].

Results and Discussion

The sample used to study the availability of boron (B), potassium (K) phosphorus (P), molybdenum (Mo), and zinc (Zn) in modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas (Table 1). This sample was chosen because it was indicated that the limestone injection process was very successful at the plant and, consequently, it is expected that modified fly ash would become available at the plant. As compared to other samples, the modified fly ash from the Kansas Power and Light Company was low in boron and potassium and intermediate in phosphorus and zinc (Table 6).

Boron greenhouse study. Application of boron as modified fly ash and as $Na_2B_4O_7 \cdot 10H_2O$ increased the yield of alfalfa on a soil that supplied inadequate amounts of the element (Table 7). The boron concentration was not as high where the modified fly ash was applied as where $Na_2B_4O_7 \cdot 10H_2O$ was applied (Table 8). This was expected for less boron was applied to the soil as modified fly ash than as $Na_2B_4O_7 \cdot 10H_2O$. The lower level of boron application as modified fly ash was felt desirable to avoid confounding effects on boron availability of high levels of pH due to application of high amounts of the by-product.

Potassium greenhouse study. Alfalfa yield was not increased by application of potassium as either potassium chloride (KCl) or modified fly ash to the Groseclose soil (Table 9). It is felt that the soil must be cropped for several cuttings before the deficiency will occur. The experiment will, therefore, be continued for several cuttings starting the fall of 1971 when conditions in the greenhouse are suitable for growing alfalfa. Application of calcium carbonate ($CaCO_3$) has been shown to decrease potassium availability in some soils[13,14]. This relationship was

not shown for the Groseclose soil by either yield of alfalfa or concentration of potassium in alfalfa tissue (Tables 9 and 10).

Molybdenum greenhouse study. Application of 42.7 grams modified fly ash increased the pH of the Cecil fine sandy loam from 5.0 to 7.5, whereas 2.1 grams of calcium carbonate increased the pH of the soil to 6.3. Neither molybdenum nor calcium carbonate application increased yield of soybeans on the acid soil (Table 11). Application of the modified fly ash decreased soybean yield. The decrease in yield probably resulted from boron toxicity or soluble salt damage as soybeans are very sensitive to both abnormalities[15].

Phosphorus greenhouse study. Application of $Ca(H_2PO_4)_2 \cdot H_2O$ to the Groseclose silt loam increased yield of corn grown in the greenhouse (Table 12). These data indicate that the soil supplied inadequate phosphorus for corn growth. Corn yield was not increased by application of 126.3 or 252.6 grams of modified fly ash. These data show that modified fly ash did not increase the phosphorus supplying power of the soil. The phosphorus concentration data show that the amount of phosphorus absorbed by corn plants was not greatly altered by application of modified fly ash (Table 13).

Zinc greenhouse study. Application of $ZnSO_4 \cdot 7H_2O$ increased corn grown on Westmorland silty clay loam (Table 14). These data show that the soil supplied an inadequate amount of zinc for corn growth. Application of elemental sulfur decreased the pH of the soil from 6.1 to 5.7. This decrease in pH probably increased the availability of residual zinc in the soil and thereby corrected zinc deficiency. Application of calcuim carbonate increased the pH of the soil from 6.1 to 6.3. This increase in pH probably decreased the availability of residual zinc in the soil and thereby resulted in the decrease in corn yield (Table 14). Application of modified fly ash did not affect corn yield. The pH of the soil was increased from 6.1 to

7.6 by application of modified fly ash. Neither the residual soil zinc nor the zinc in modified fly ash would be expected to have high availability at a soil pH of 7.6. The zinc concentration data (Table 15) closely parallel yield data (Table 14).

SUMMARY

The results of this research show two possible beneficial effects from application of modified fly ash to agricultural soils. That is, application of modified fly ash increases the boron supplying power and pH of soils. Increasing the pH of acidic soils increases yield of certain crops.

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Table 1. Samples of fly ash under study.

Sample No.	Source
1	Drummond Island, dolomite modified, wet-collected fly ash (D.W.)
2	Presque Isle, limestone modified, dry-collected fly ash (P.I.D.)
3	Chevrolet Motor Division Plant, St. Louis, Missouri; dolomite injected, dry-collected fly ash (C.I.)
4	Chevrolet Motor Division Plant, St. Louis, Missouri; unmodified fly ash (C.U.)
5	Kansas Power and Light Company, Lawrence, Kansas; limestone injected, wet-collected fly ash (K.P.L.)
6	Chevrolet Motor Division Plant, St. Louis, Missouri; dolomite premixed, dry-collected fly ash (C.M.)

Table 2. The pH of three soils as related to levels of calcium carbonate ($CaCO_3$) application.

Treatment	Soil type		
	Davidson clay loam	Marlboro fine sandy loam	Tatum silt loam
mg $CaCO_3$/30g soil			
0	5.0	4.9	4.4
30	5.4	5.8	4.8
60	6.0	6.4	5.1
90	6.3	6.9	5.4
120	6.5	7.1	5.9
150	6.8	7.4	6.3
180	6.8	7.5	7.2
210	7.0	7.6	7.4

Table 3. The pH of three soils as related to levels of modified fly ash application.

Treatment		Soil type		
Modified fly ash	Level of application	Davidson clay loam	Marlboro fine sandy loam	Tatum silt loam
	mg/30g soil			
DW	300	6.3	6.6	4.9
	1800	7.8	8.4	7.8
PID	300	6.8	7.6	6.2
	1800	8.2	8.6	8.6
CI	300	7.1	8.1	6.7
	1800	8.0	8.9	7.9
CU	300	5.4	5.4	4.2
	1800	6.7	7.9	5.8
KPL	300	6.0	6.4	4.9
	1800	7.7	8.0	7.5
CM	300	6.8	7.6	6.0
	1800	7.8	8.6	8.1

Table 4. Neutralizing power of modified fly ash determined by titration procedures.

Modified fly ash	Neutralizing Power
	meq H_3O^+/g
DW	2.8
PID	8.0
CI	9.2
CU	1.9
KPL	1.9
CM	10.4

Table 5. The concentrations of aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg) in modified flyash.

Modified Flyash	Concentration (%) of			
	Al	Ca	Fe	Mg
DW	6.1	10.9	5.2	4.8
PID	8.2	20.5	3.8	1.1
CI	5.1	16.1	4.6	8.3
CU	9.8	4.6	7.3	1.4
KPL	12.3	16.0	8.2	1.3
CM	6.9	15.4	4.4	8.2

Table 6. The concentrations of boron (B), potassium (K), phosphorous (P) and zinc (Zn) in modified fly ash.

Modified fly ash	Concentration of			
	B	K	P	Zn
	ppm	%	ppm	ppm
DW	253	0.57	875	81
PID	673	0.97	1550	135
CI	740	0.63	250	294
CU	993	1.02	250	480
KPL	48	0.71	625	353
CM	923	0.76	425	359

Table 7. Yield of alfalfa as related to application of boron (B) as $Na_2B_4O_7 \cdot 10H_2O$ and as modified fly ash.

Treatment*	Yield**
	g/pot
Check	6.0b
27.9 mg $Na_2B_4O_7 \cdot 10H_2O$	7.1a
55.8 mg $Na_2B_4O_7 \cdot 10H_2O$	7.0a
7.6 g modified fly ash	7.1a
22.8 g modified fly ash	7.2a

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

**Means followed by different letters are significantly different at the 5% level of probability.

Table 8. The boron (B) concentration of alfalfa tissue as related to application of boron as $Na_2B_4O_7 \cdot 10H_2O$ and as modified fly ash.

Treatment*	B concentration
	ppm
Check	9.7
27.9 mg $Na_2B_4O_7 \cdot 10H_2O$	151.0
55.8 mg $Na_2B_4O_7 \cdot 10H_2O$	149.5
7.6 g modified fly ash	31.0
22.8 g modified fly ash	44.0

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

Table 9. Yield of alfalfa as related to application of potassium (K) as potassium chloride and as modified fly ash.

Treatment*	Yield**
	g/pot
Check	7.4
200.5 mg KCl	7.6
2.1 g $CaCO_3$	7.6
200.5 mg KCl, 2.1 g $CaCO_3$	7.9
3.4 g modified fly ash	8.4
13.6 g modified fly ash	7.7

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

**Differences in yield were not significant at the 5% level of probability.

Table 10. The potassium (K) concentration of alfalfa tissue as related to application of potassium as potassium chloride and as modified fly ash.

Treatment*	K concentration
	%
Check	1.6
200.5 mg KCl	2.6
2.1 g $CaCO_3$	1.5
200.5 mg KCl, 2.1 g $CaCO_3$	2.3
3.4 g modified fly ash	1.5
13.6 g modified fly ash	1.6

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

Table 11. Yield of soybeans as related to application of molybdenum (Mo) as $Na_2MoO_4 \cdot 2H_2O$ and as modified fly ash.

Treatment*	Yield**
	g/pot
Check	12.7a
2.12 mg $Na_2MoO_4 \cdot 2H_2O$	12.1a
4.24 mg $Na_2MoO_4 \cdot 2H_2O$	12.8a
2.1 g $CaCO_3$	13.0a
2.1 g $CaCO_3$, 2.12 mg $Na_2MoO_4 \cdot 2H_2O$	12.4a
42.7 g modified fly ash	11.0b

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

**Means followed by different letters are significant at the 5% level of probability.

Table 12. Yield of corn as related to application of phosphorus (P) as $Ca(H_2PO_4)_2 \cdot H_2O$ and as modified fly ash.

Treatment*	Yield**
	g/pot
Check	8.0b
854 mg $Ca(H_2PO_4)_2 \cdot H_2O$	18.8a
2.1 g $CaCO_3$	8.6b
2.1 g $CaCO_3$, 854 mg $Ca(H_2PO_4)_2 \cdot H_2O$	17.9a
126.3 g modified fly ash	9.3b
252.6 g modified fly ash	3.0c

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

**Means followed by different letters are significantly different at the 5% level of probability.

Table 13. The phosphorous (P) concentration of corn tissue as related to application of phosphorous as $Ca(H_2PO_4)_2 \cdot H_2O$ and as modified fly ash.

Treatment*	P concentration
	%
Check	0.14
854 mg $Ca(H_2PO_4)_2 \cdot H_2O$	0.21
2.1 g $CaCO_3$	0.16
2.1 g $CaCO_3$, 854 mg $Ca(H_2PO_4)_2 \cdot H_2O$	0.24
126.3 g modified fly ash	0.22
252.6 g modified fly ash	0.21

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

Table 14. Yield of corn as related to application of zinc (Zn) as $ZnSO_4 \cdot 7H_2O$ and as modified fly ash.

Treatment*	Yield**
	g/pot
Check	11.2b
83.3 mg $ZnSO_4 \cdot 7H_2O$	15.9a
1.0 g elemental sulfur	15.5a
2.1 g $CaCO_3$	7.5c
2.1 g $CaCO_3$, 83.3 mg $ZnSO_4 \cdot 7H_2O$	15.4a
165.1 g modified fly ash	9.4bc

*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

**Means followed by different yields are significantly different at the 5% level of probability.

Table 15. The zinc (Zn) concentration of corn tissue as related to application of zinc as $ZnSO_4 \cdot 7H_2O$ and as modified fly ash.

Treatment*	Zn concentration
	ppm
Check	14.7
83.3 mg $ZnSO_4 \cdot 7H_2O$	19.0
1.0 g elemental S	13.3
2.1 g $CaCO_3$	15.3
2.1 g $CaCO_3$, 83.3 mg $ZnSO_4 \cdot 7H_2O$	21.3
165.1 g modified fly ash	20.0

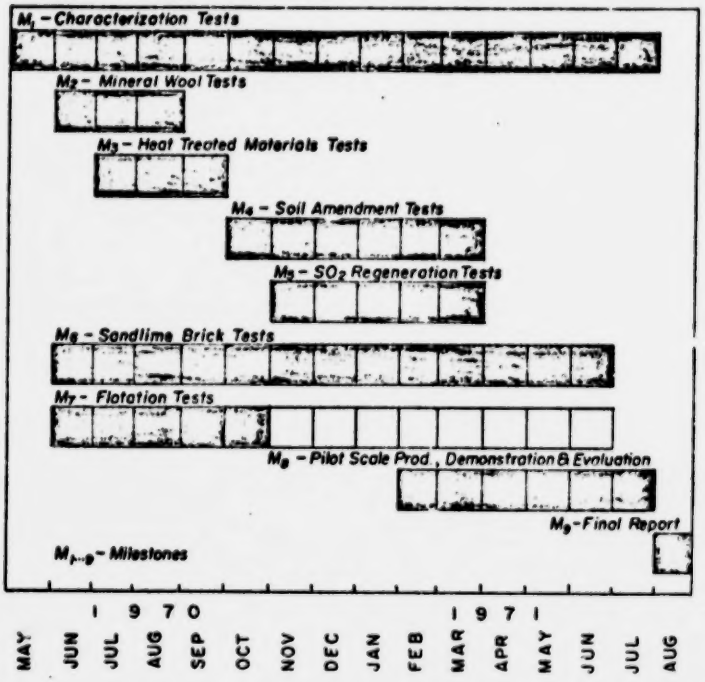
*The modified fly ash was obtained from the Kansas Power and Light Company, Lawrence, Kansas.

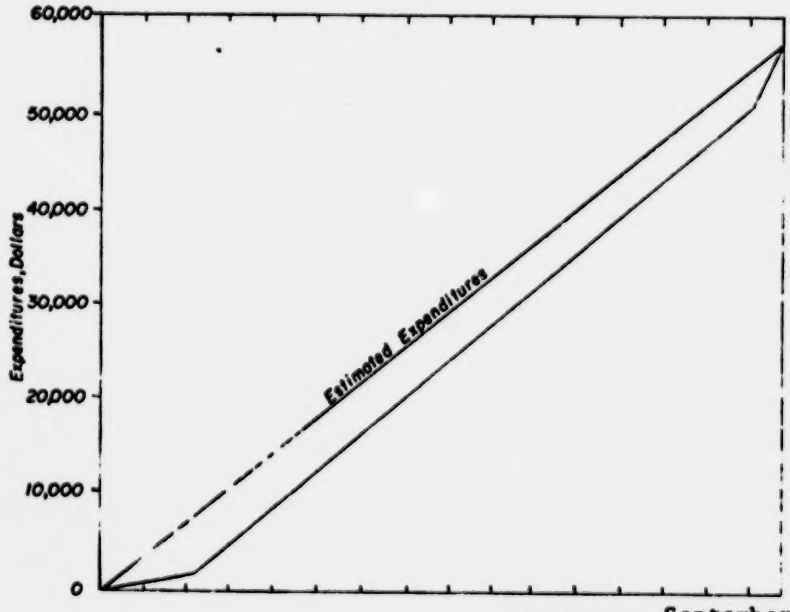
CONTRACT: PILOT SCALE-UP OF PROCESSES TO DEMONSTRATE UTILIZATION OF PULVERIZED COAL FLYASH MODIFIED BY THE ADDITION OF LIMESTONE-DOLOMITE SULFUR DIOXIDE REMOVAL ADDITIVES.

CONTRACTOR: COAL RESEARCH BUREAU, WEST VIRGINIA UNIVERSITY

CONTRACT NO. CPA 70-66 Contractor Project Off.: J.W. Leonard

CONTRACT DATES- 5/1/70-8/30/71 NAPCA Proj. Off.: T.A. Kittleman


M1 - Characterization Tests
M2 - Mineral Wool Tests
M3 - Heat Treated Materials Tests
M4 - Soil Amendment Tests
M5 - SO2 Regeneration Tests
M6 - Sandlime Brick Tests
M7 - Flotation Tests
M8 - Pilot Scale Prod., Demonstration & Evaluation
M9 - Final Report
M1-9 - Milestones
1970
1971
MAY JUN JUL AUG SEP OCT NOV DEC JAN FEB MAR APR MAY JUN JUL AUG



PROGRESS TO September 30, 1971